

*Photon In - Photon Out Techniques for Studies  
of Surface Structures and Dynamics at  
Interfaces*

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and

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# Challenge!

Detect Properties of  
 $10^{13} - 10^{15}$  Surface Atoms ( $\text{cm}^{-2}$ )

In the Presence of  
 $10^{22}$  Bulk Atoms ( $\text{cm}^{-3}$ )

# Structure and Dynamics at Buried Interfaces

- Solid - High Pressure Gas  
Catalysis
- Solid - Liquid  
Biology, Electrochemistry
- Solid - Solid  
Tribology

# Challenges for the ALS

Develop Photon In - Photon Out Techniques for Studies of

- Monolayers of Nanoparticles
- Peptide and Protein Monolayers at Polymer-Water Interfaces
- Better Time Resolution
- Better Spatial Resolution

# **Surface Techniques**

## **Photon Scattering**

X-Ray Absorption Spectroscopy, GrazingangleDiffractions; Infrared Spectroscopies; Raman Spectroscopies; Microscopy; Sum Frequency Generation -Surface Vibrational Spectroscopy; Nuclear Magnetic Resonance

## **Electron Scattering**

Photoelectron Spectroscopy, Microscopy; Extended X-Ray Absorption Fine Structures, Techniques; Low Energy Electron Diffraction; Electron Microscopy

## **Ion Scattering**

Ion Scattering Spectroscopies; Secondary Ion Mass Spectroscopy; Field ion Microscopy

## **Scanning Probes**

Scanning Tunneling Microscopy; Atomic Force Microscopy

## **Atomic and Molecular Beam Scattering**

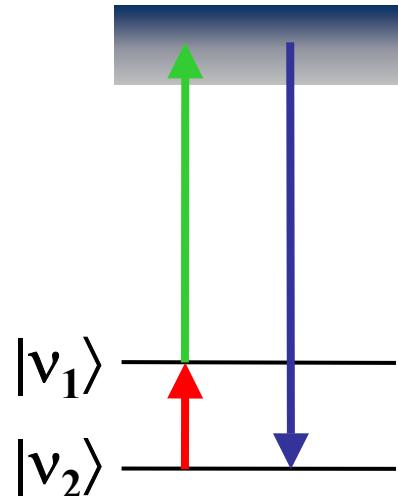
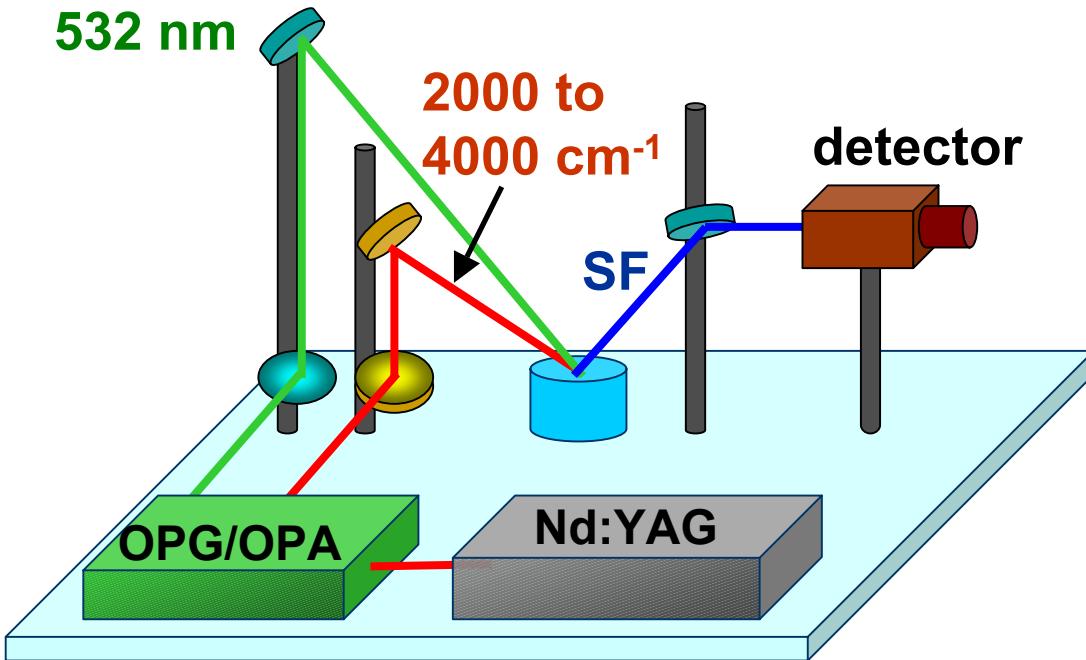
Diffraction, Energy Transfer

## **Isotope Techniques**

<sup>14</sup> C, Positron emission

## **Adsorption, Desorption**

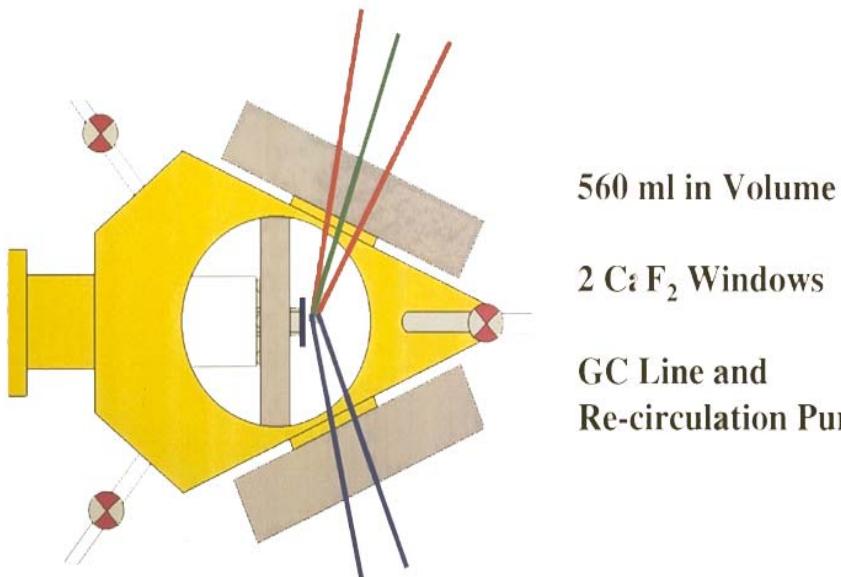
# Sum-Frequency Generation: An *in situ* Surface-specific Vibrational Spectroscopy



Random and isotropic  
materials *do not*  
generate SFG

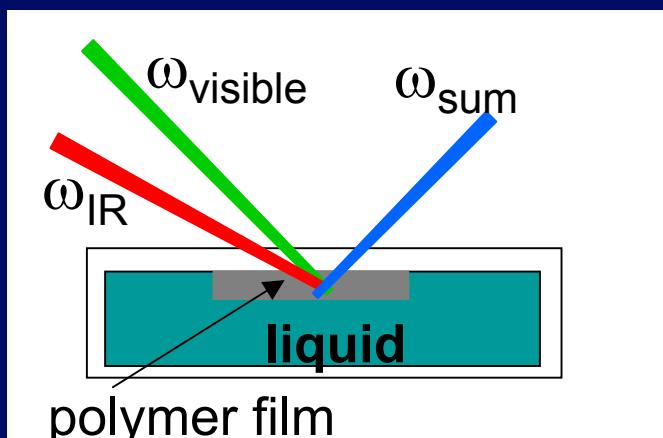
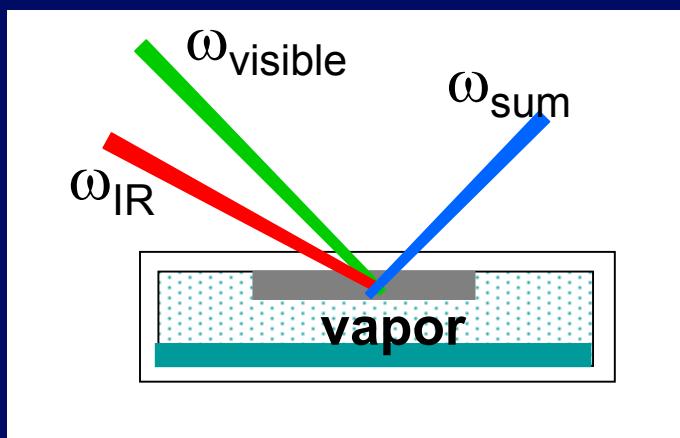
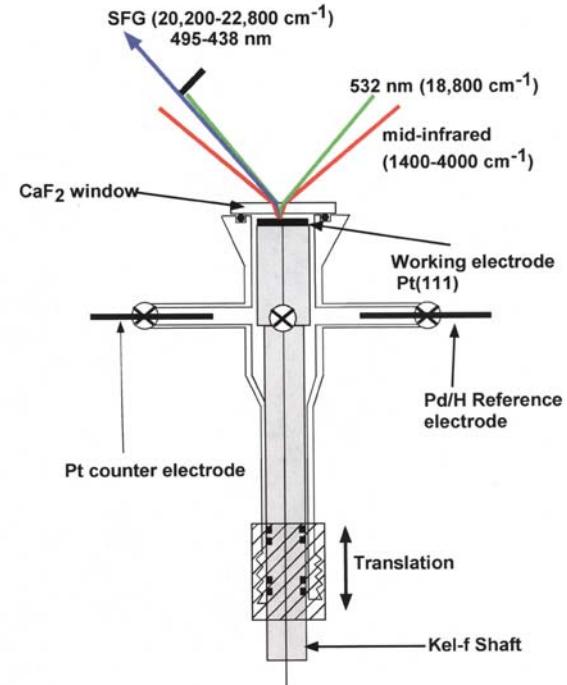
Vibrations must obey  
both IR and Raman  
selection rules

# Top View of Reaction Cell



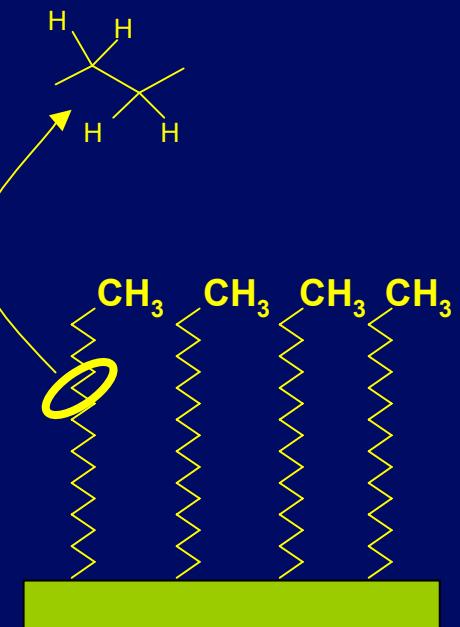
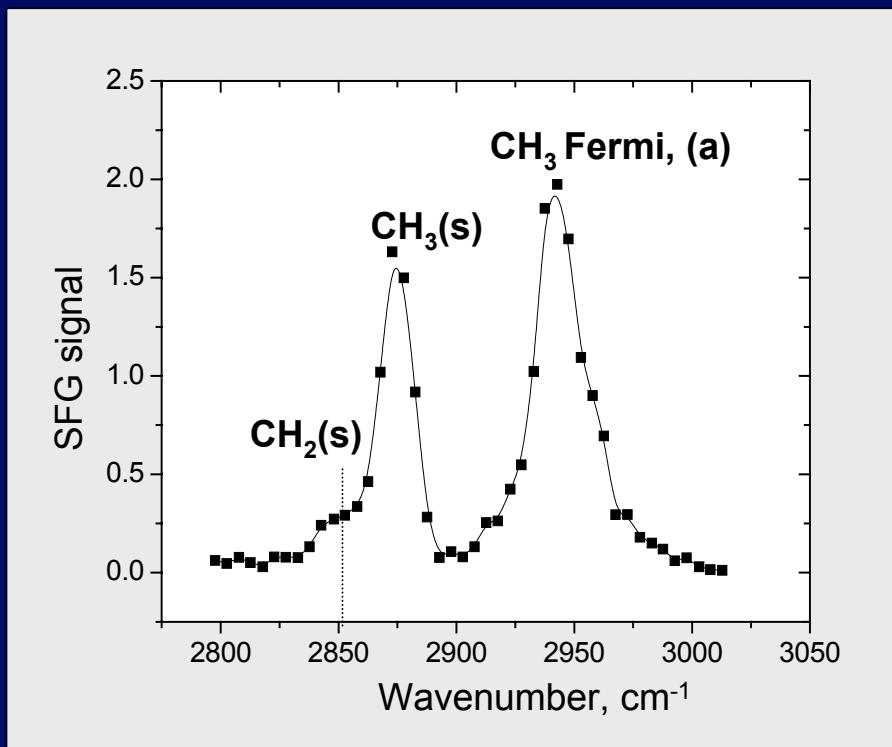
Polymer/vapor and polymer/liquid interfaces

Thin-layer Electrochemical Cell for Sum FrequencyGeneration (SFG) Surface Vibrational Spectroscopy.

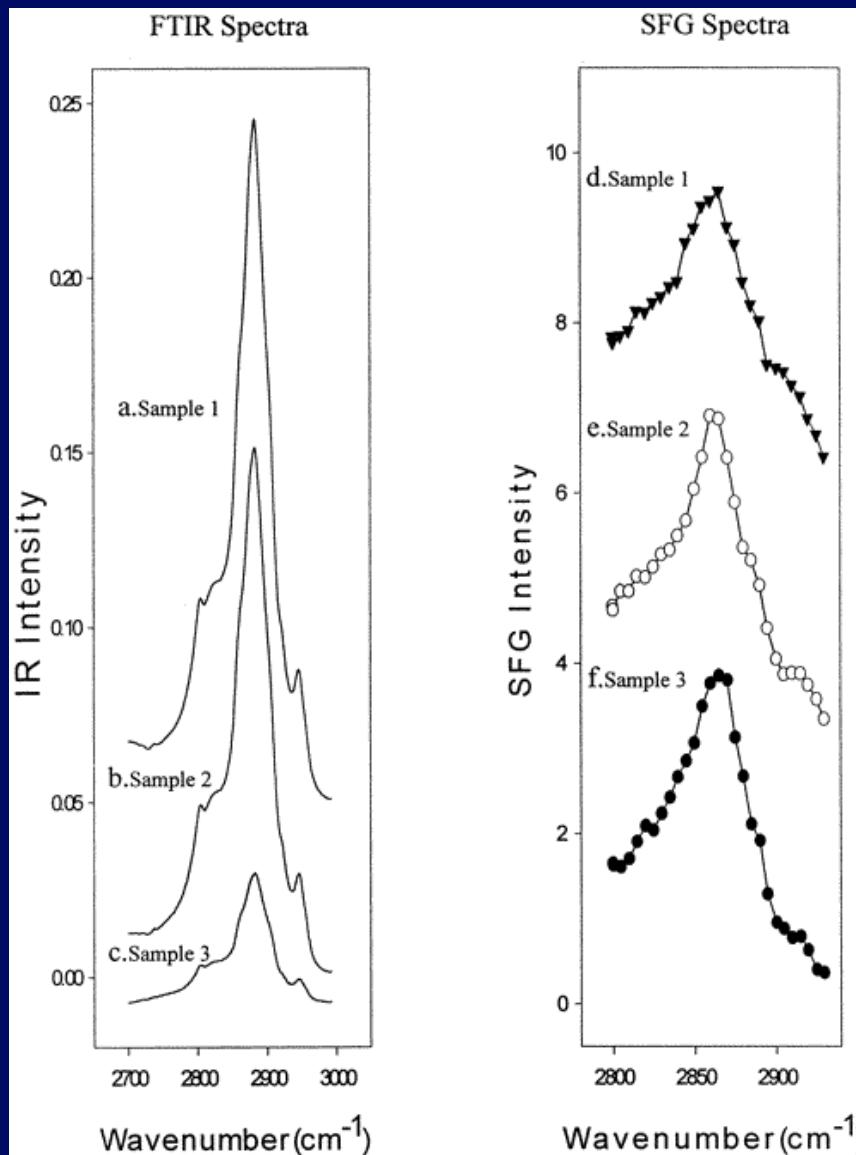


# Example: Alkanethiol self-assembled monolayer (SAM)

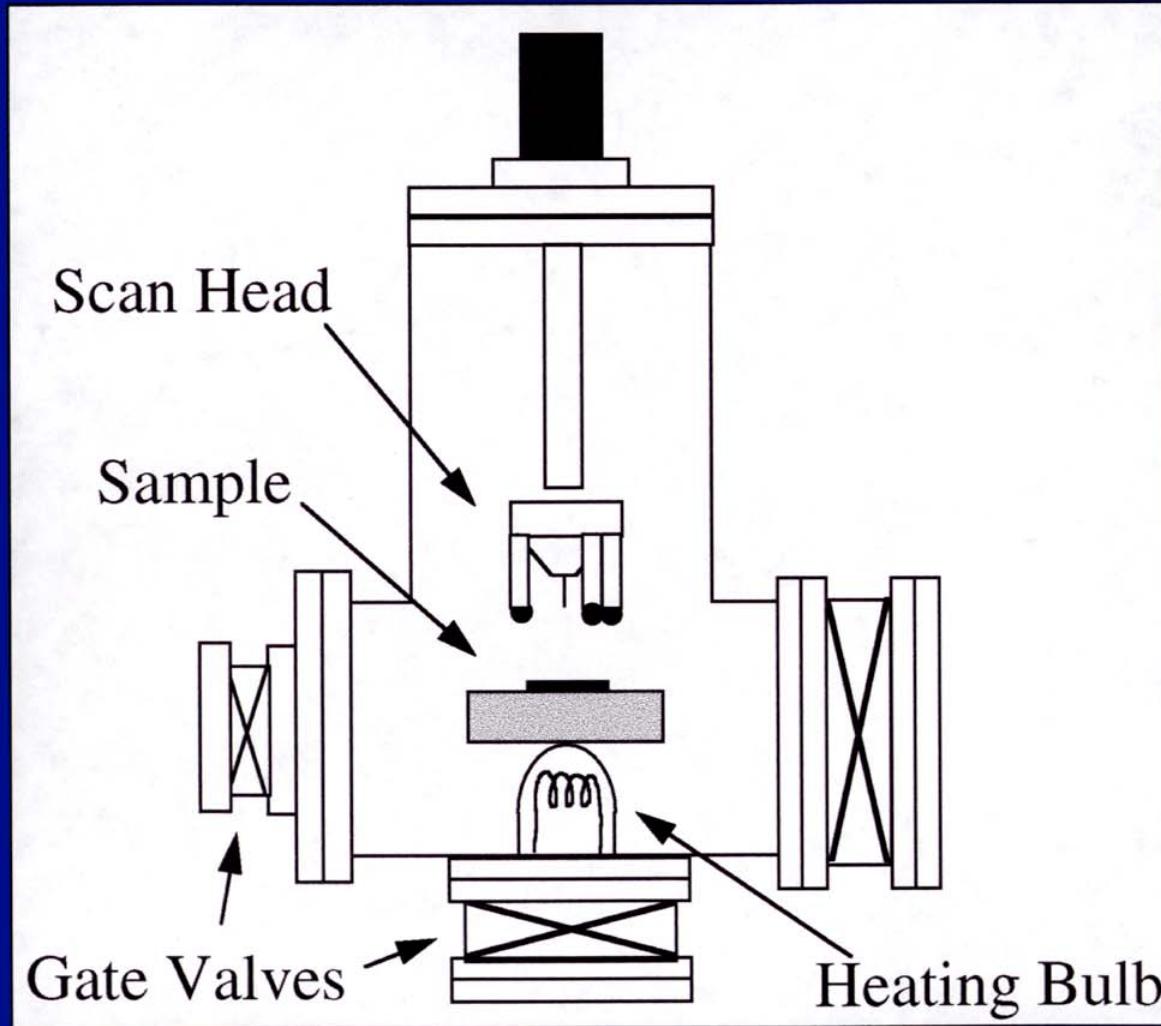
SFG spectra: C-H stretching region



# Comparison of the SFG and FTIR spectra generated from different thickness polyethylene glycol films



# The High Pressure - High Temperature STM

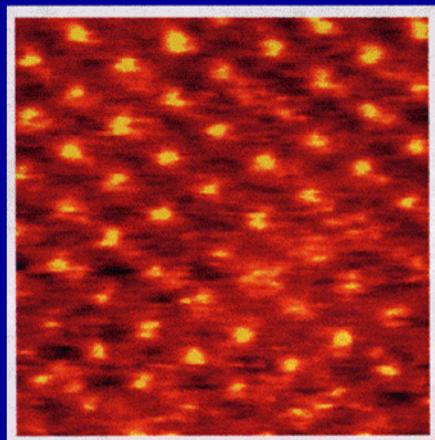


Pressure range:  
 $5 \times 10^{-10}$  torr to 1 atm

Temperature range:  
25 °C to 400 °C

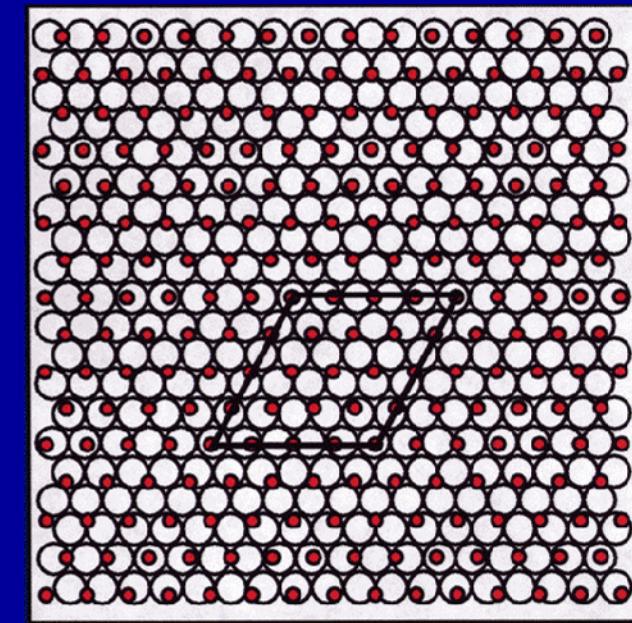
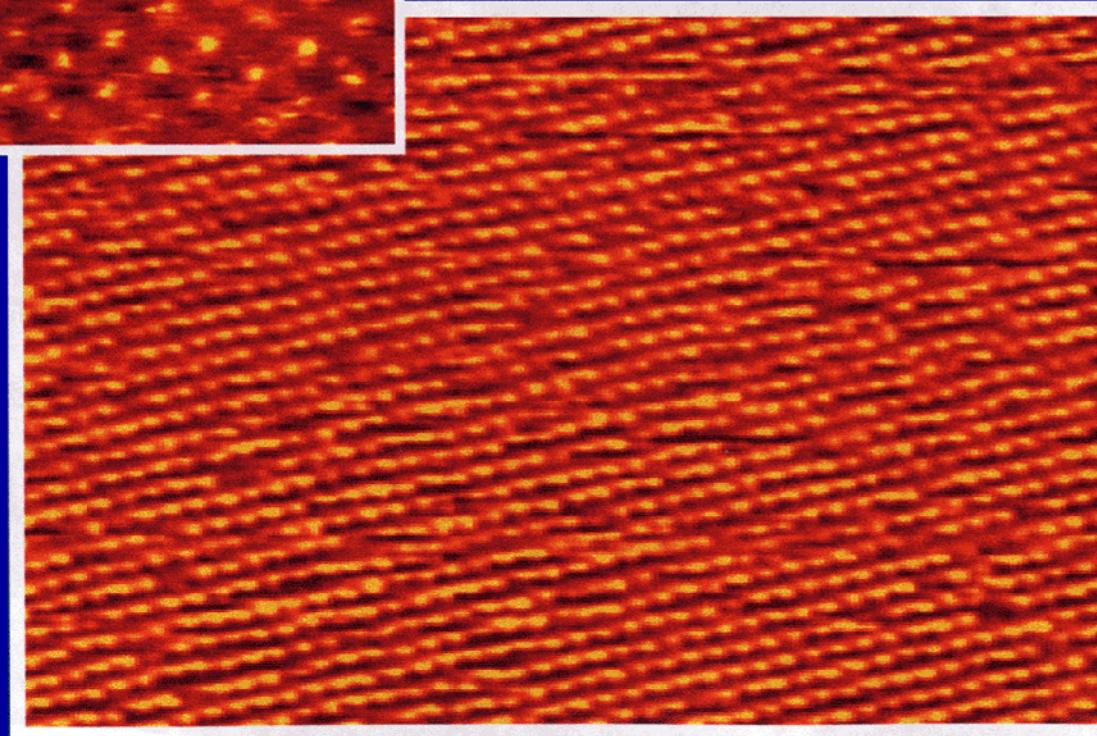
# High Pressure CO Structure on Pt(111)

Not Seen at Low Pressure



$P_{CO} = 150$  torr

25 Å



250 Å

● CO molecule  
○ Pt atom

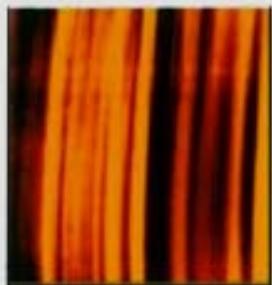
approximately  
 $(5 \times 5)$

# Adsorbate Induced Restructuring

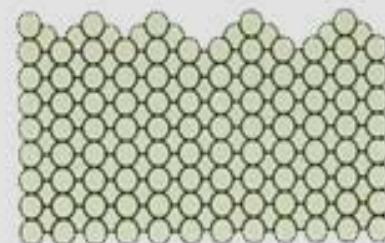
# *In Situ* High Pressure STM

## Adsorbate-induced surface reconstructions

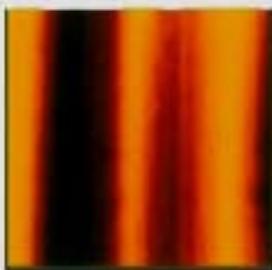
### Pt(110) under atmospheric pressures



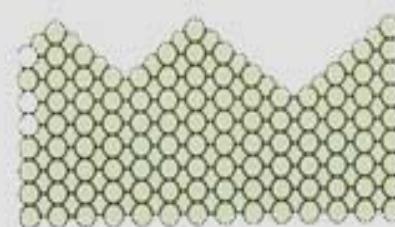
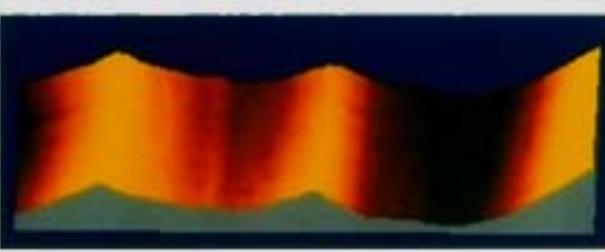
hydrogen: 1.7 atm. 730 Å x 700 Å.



"nested" missing-row reconstructions.



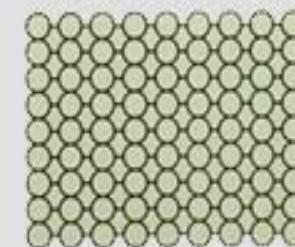
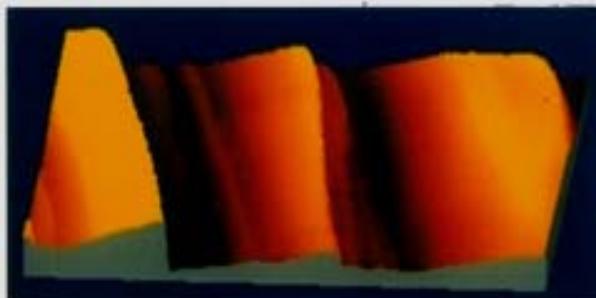
oxygen: 1 atm. 900 Å x 780 Å.



(111) microfacets.



carbon monoxide: 1 atm. 770 Å x 740 Å.



[110]  
[110]  
[001]

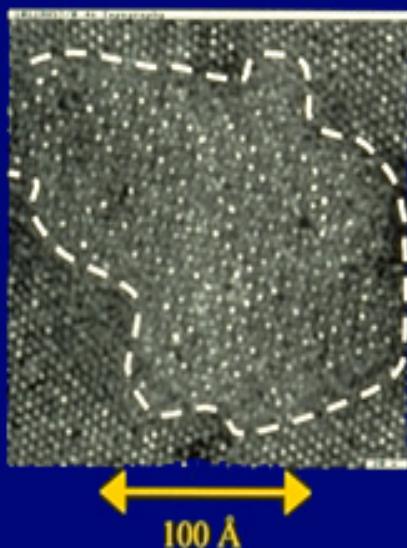
unreconstructed (1x1) terraces  
separated by multiple height steps.

# Adsorption Isotherm

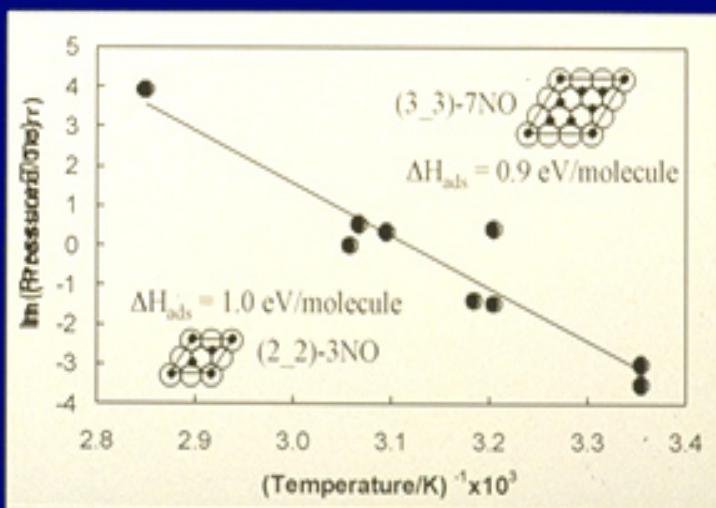
Langmuir

$$\sigma = \frac{\sigma_0 b P}{\sigma_0 + b P} \quad \Theta = \frac{\sigma}{\sigma_0}$$

STM (2x2) ⇌ (3x3) NO



Phase Diagram



# Energy Conversion Strategies

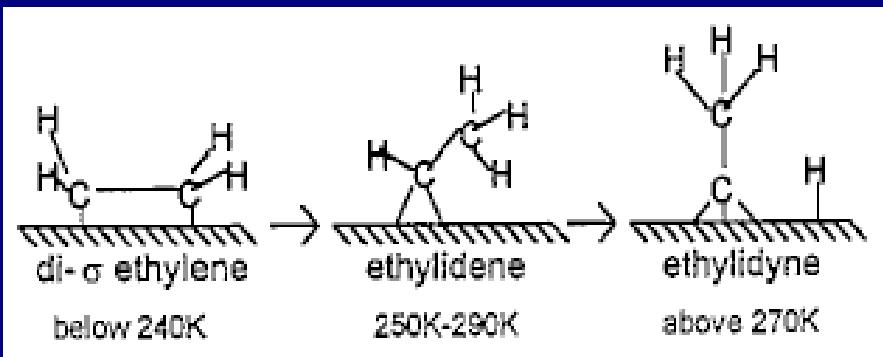
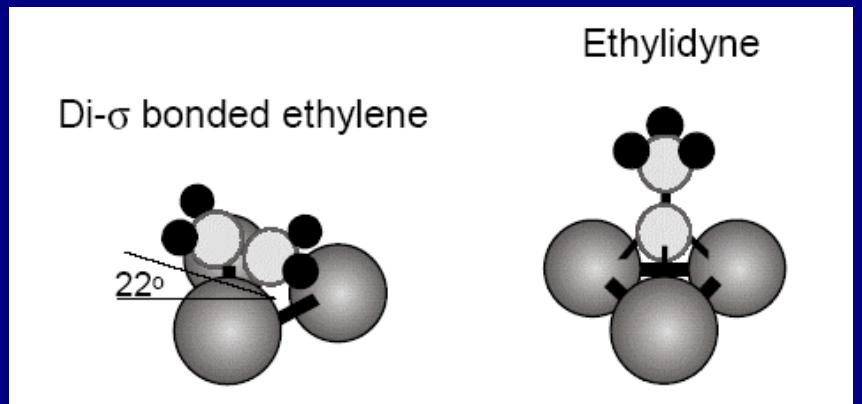
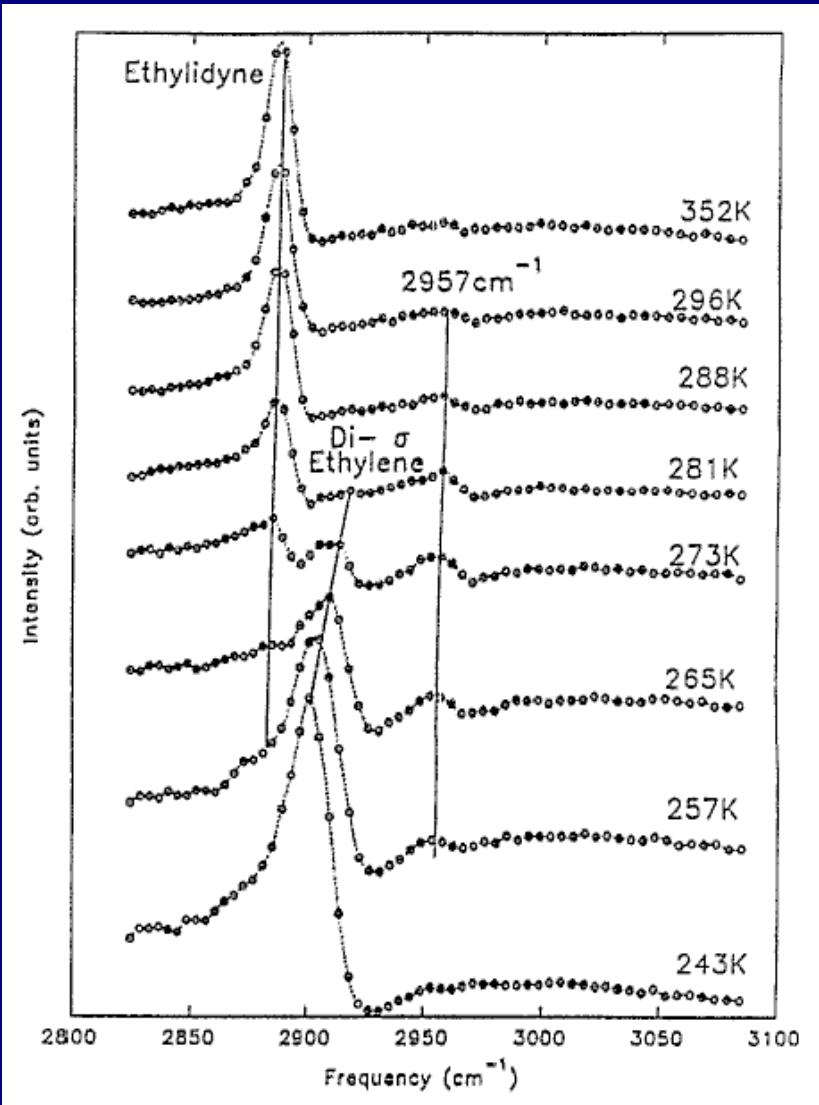
Bond Activation

C-H, C=O, O-H, N≡N, N-H

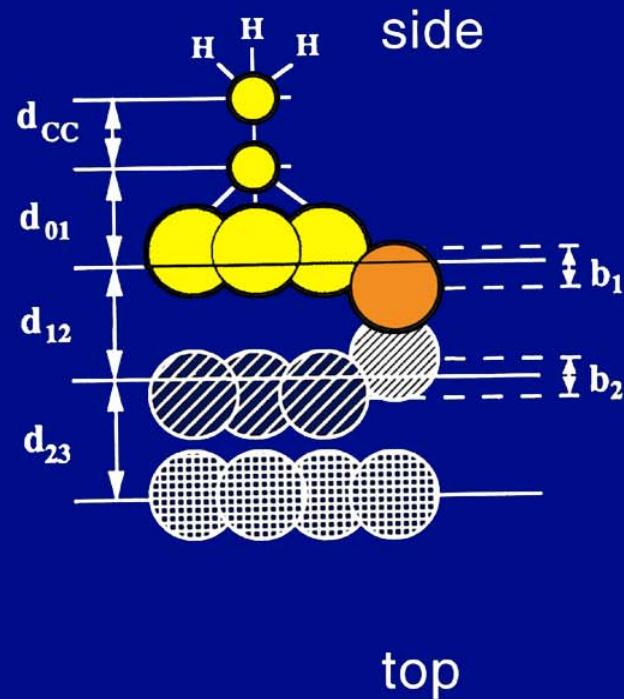
# C-H Activation in Alkenes and Alkanes on Pt(111)

Alkenes (pressure < 10 <sup>-6</sup> Torr)	C-H Dissociation Temperature
Ethylene	250 K
Propylene	230 K
Isobutene	270 K
1-Hexene	250 K
Cyclohexene	200 K
Alkanes (pressure 1-1.5 Torr)	
Methane	250 K
Ethane	275 K
n-Hexane	296 K
2-Methylpentane	296 K
3-Methylpentane	296 K

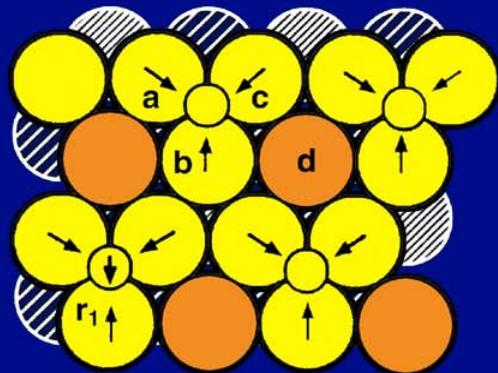
# C-H Activation in Ethylene on Pt(111) at Low Pressures ( $10^{-7}$ Torr)



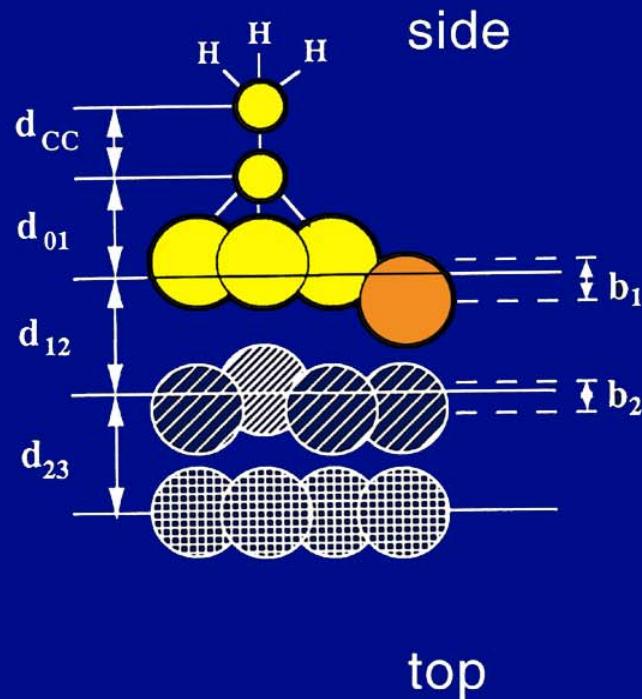
Pt(111) - (2 × 2) - C<sub>2</sub>H<sub>3</sub>



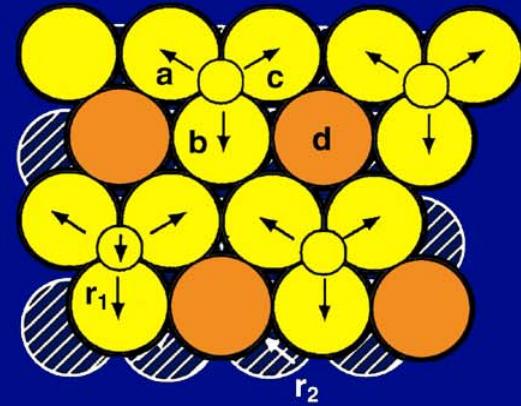
$$r_1 = 0.1 \pm 0.08 \text{ \AA}$$
$$r_2 = 0.0 \pm 0.09 \text{ \AA}$$



Rh(111) - (2 × 2) - C<sub>2</sub>H<sub>3</sub>



$$r_1 = 0.01 \pm 0.06 \text{ \AA}$$
$$r_2 = 0.00 \pm 0.07 \text{ \AA}$$





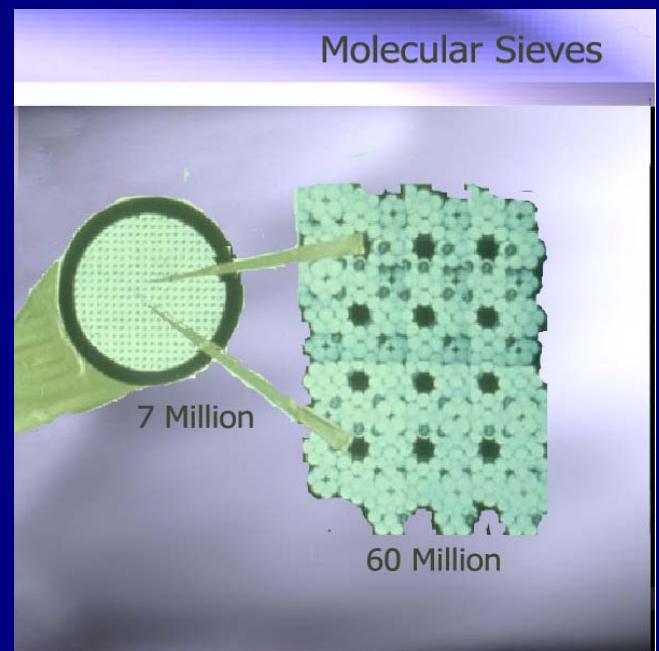
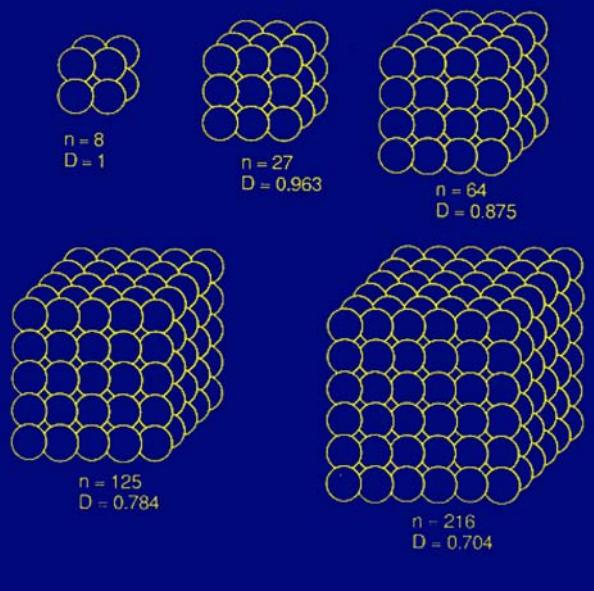
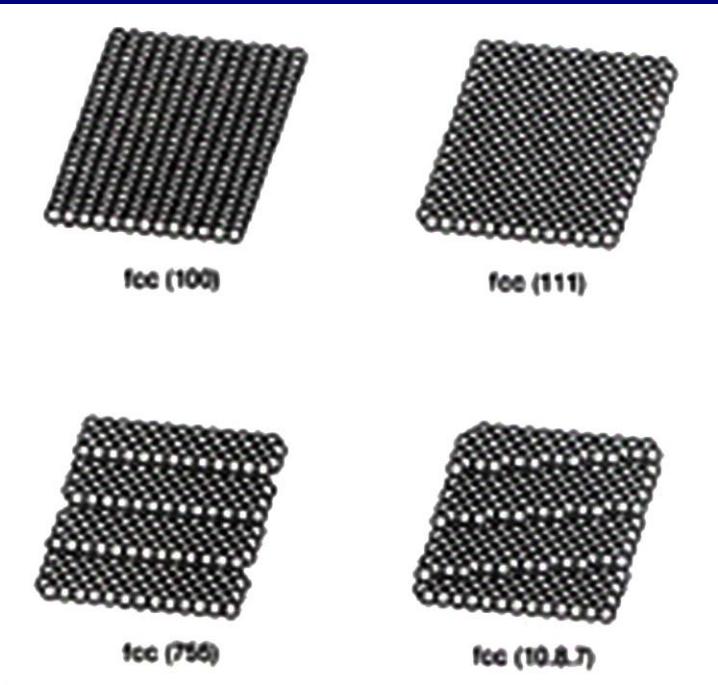
Flat surfaces



Heat to order



Repeat to grow ordered thin films layer by layer



# Catalysis in the 21st Century

100% Selectivity for  
All Catalyst-Based Processes

# Technically and Biologically Important Length Scales

## Intel Processors

P 4

P 3

486DX

8088

4004



2003

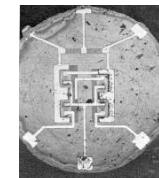
1999

1989

1981

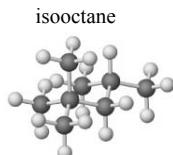
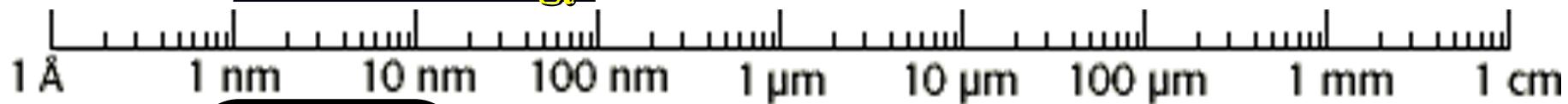
1969

## First Fairchild IC

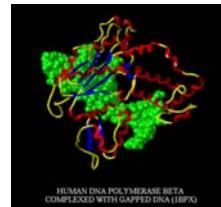


1961

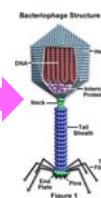
## Nanotechnology



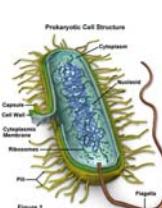
Hydrocarbon  
Fuel of today



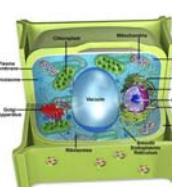
Enzyme



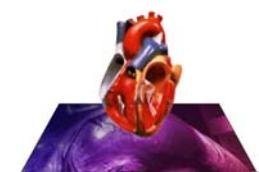
Virus



Bacterium



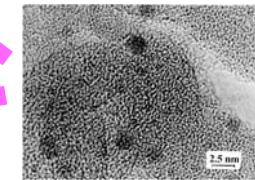
Animal Cell



Plant Cell

Tissue & Organ

H<sub>2</sub> - Fuel  
of tomorrow



Pt/SiO<sub>2</sub> catalyst

Catalysis

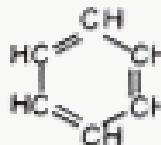
*Catalysis is an integral part of nanotechnology. Biological catalysts – enzymes – are the foundation of biological systems, while synthetic heterogeneous catalysts – metal or metal oxide nanoparticles supported on oxides – are the foundation of the chemical industry.*

# Reforming with Pt Catalyst

Octane  
Rating

110

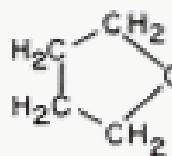
AROMATIZATION



+ 4 H<sub>2</sub>

benzene

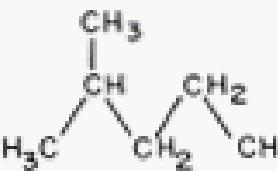
CYCLIZATION



methylcyclopentane

93

ISOMERIZATION



2-methyl pentane

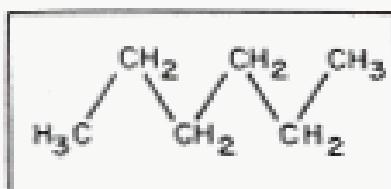
78

HYDROGENOLYSIS



propane

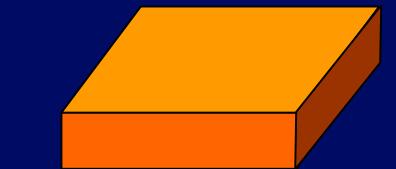
N/A



n - hexane

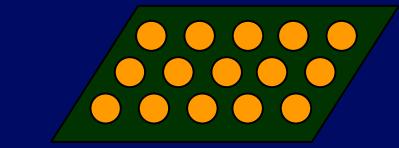
Platinum  
Catalyst  
Excess H<sub>2</sub>  
500-750K

# Evolution of the Model Catalysts System



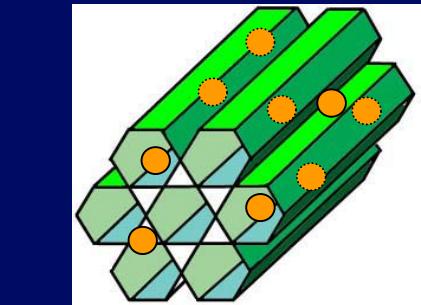
Pt single crystal

surface structure control

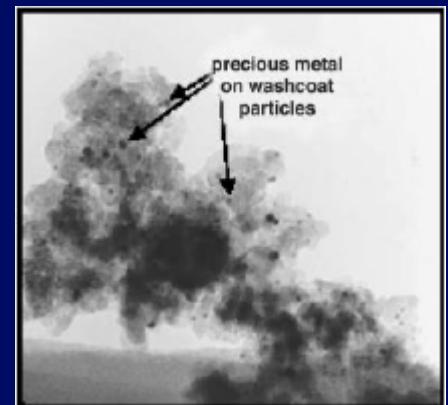


2D Pt nanoparticle array

size, interfacial area control

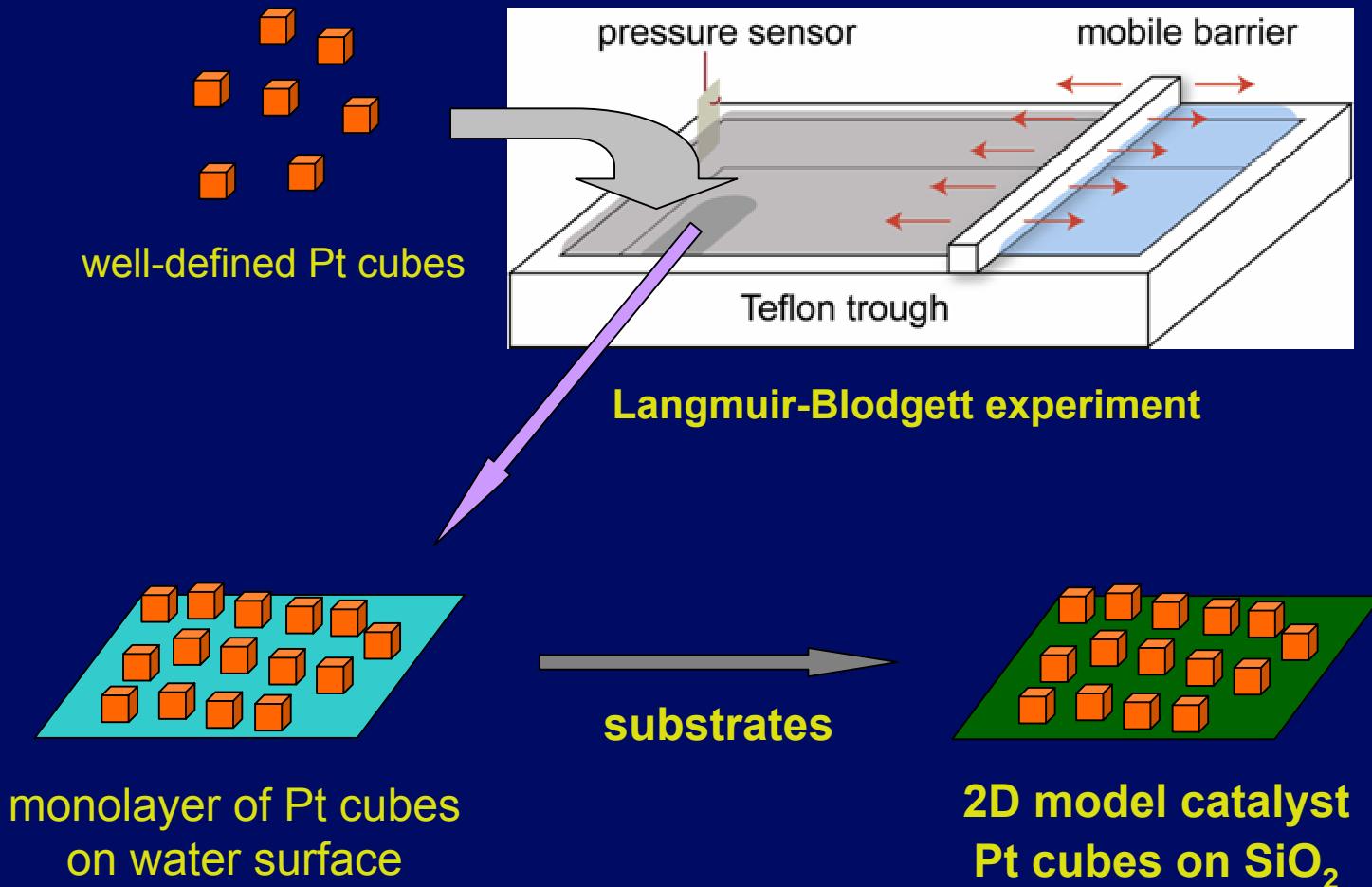


3D Pt nanoparticle array on high surface area supports

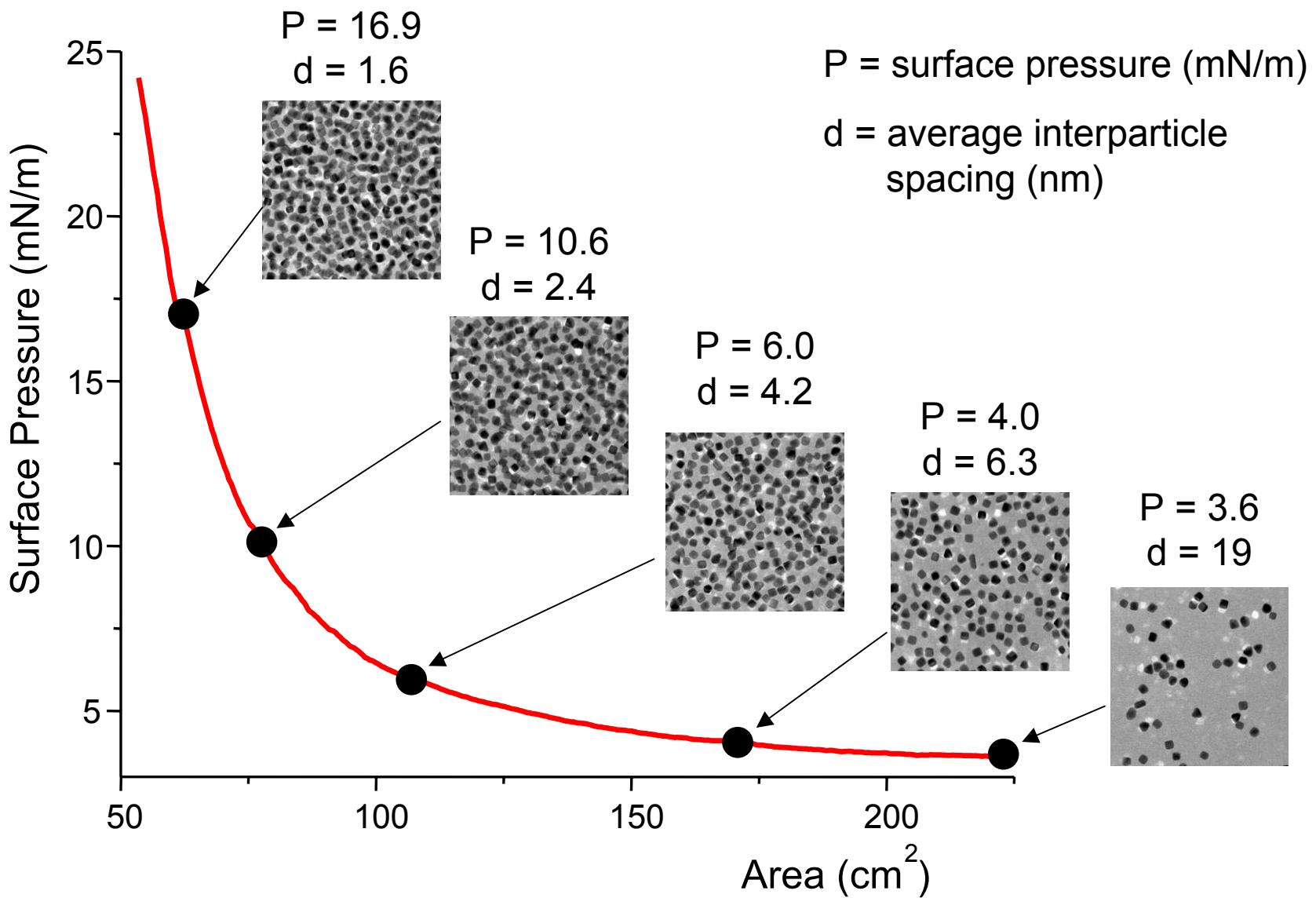


real catalysts

# Strategy for 2D model catalyst system

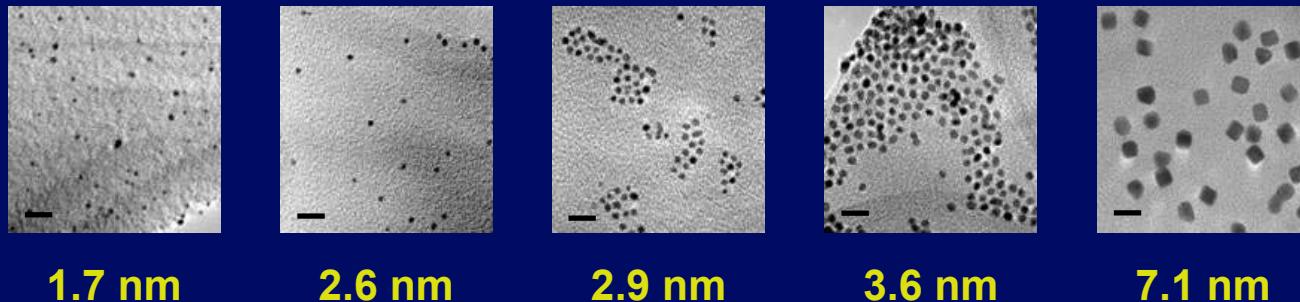


- Density control of the monolayer

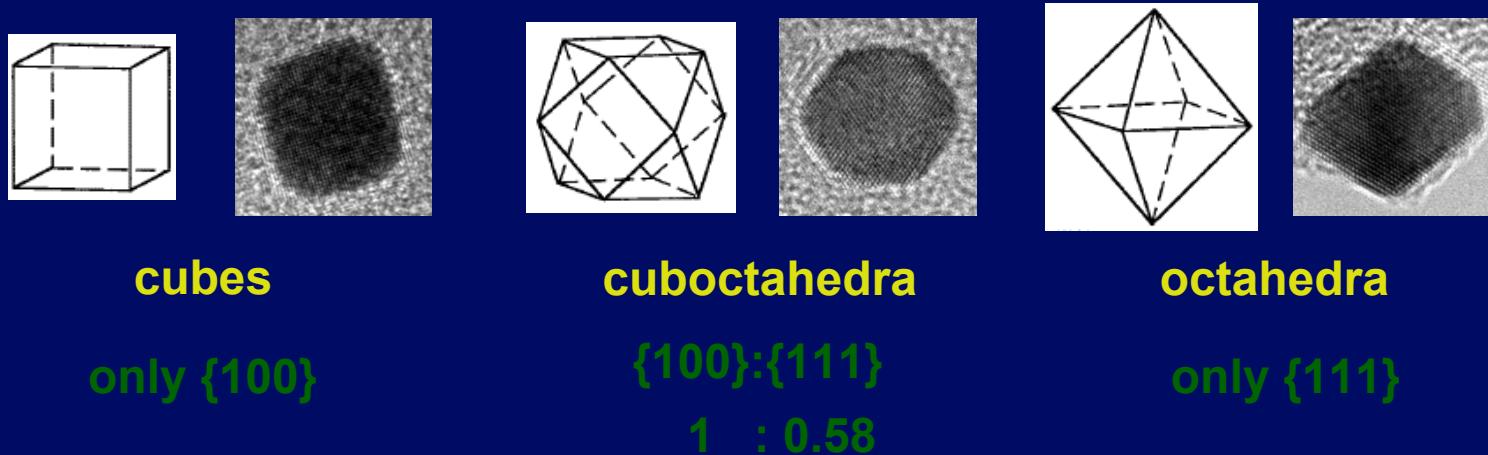


# Strategy for 2D model catalyst system

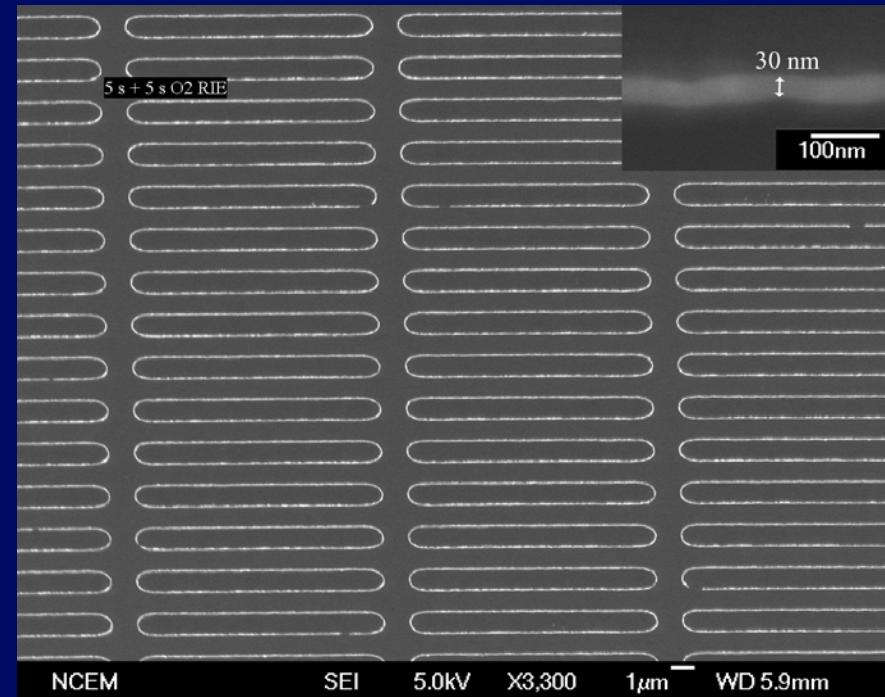
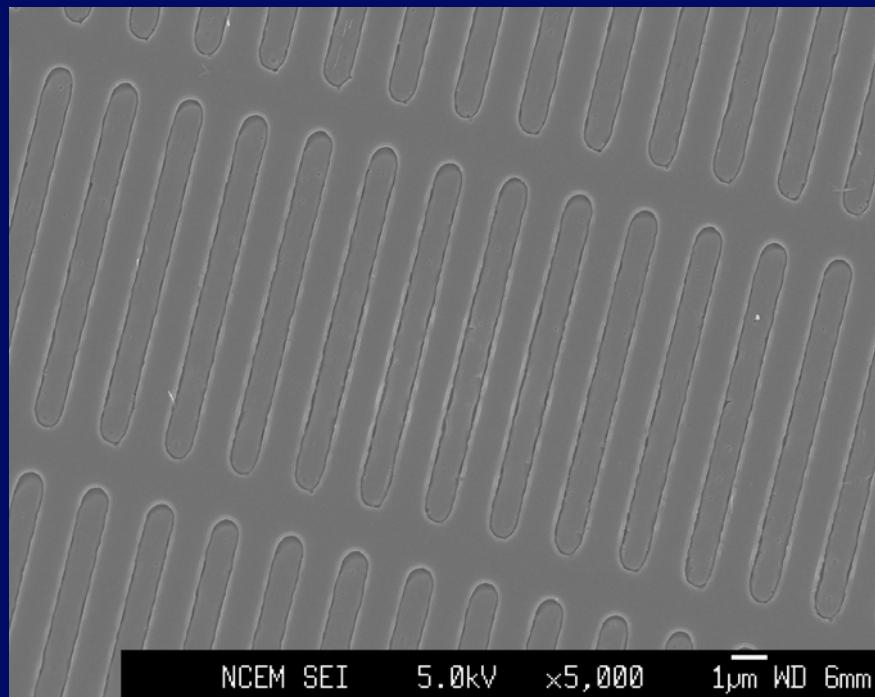
- Size dependency of the reaction



- Shape and surface structure dependency of the reaction



# Pt Nanowire High-tech Catalyst After Liftoff



PMMA After Imprinting

30 nm Pt nanowire after liftoff

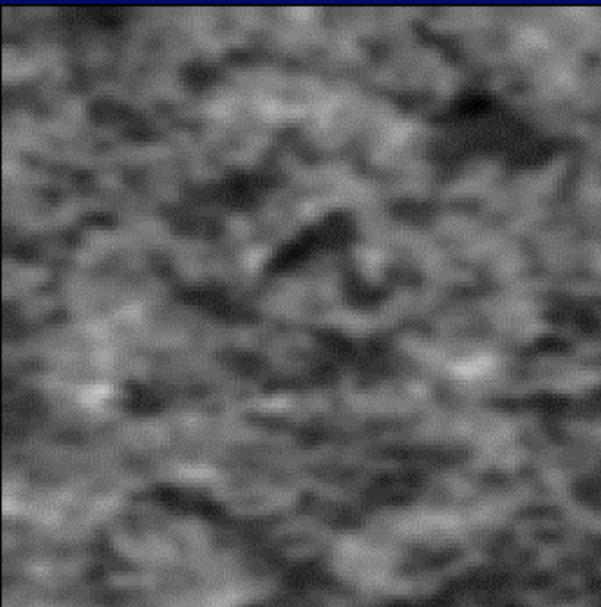
# ALS Studies of the Surface Structure of Nanoparticles and Nanowires

# Surface Dynamics with the ALS

# The Chemically Active Surface is Mobile

- Adsorbate Induced Restructuring of Metal Atoms
- Strongly Adsorbed Atoms or Molecules are Mobile

# CO Poisons Ethylene Hydrogenation and Induces Surface Order on Rh(111)



20 mTorr H<sub>2</sub>

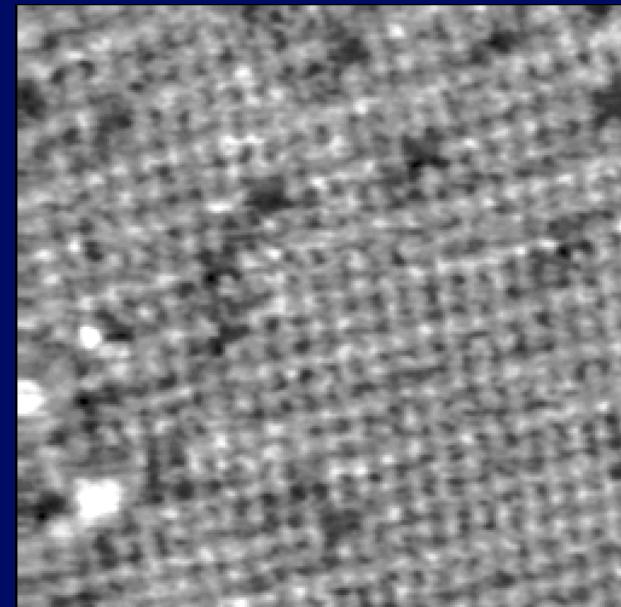


20 mTorr H<sub>2</sub>

+

20 mTorr C<sub>2</sub>H<sub>4</sub>

(100 Å)<sup>2</sup> images



20 mTorr H<sub>2</sub>

+

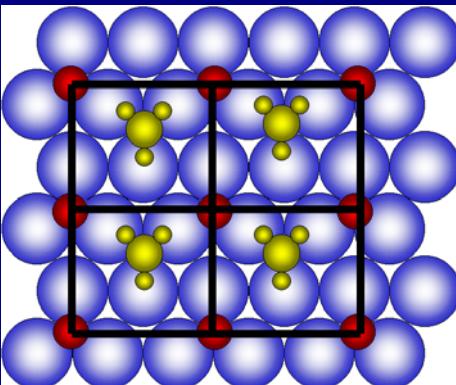
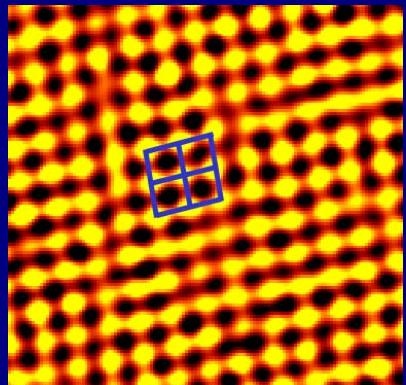
20 mTorr C<sub>2</sub>H<sub>4</sub>

+

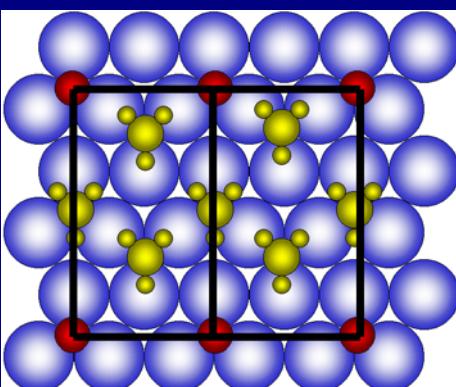
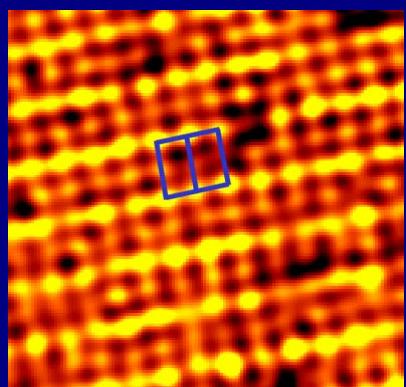
5.6 mTorr CO

QuickTime™ and a Sorenson Video decompressor are needed to see this picture.

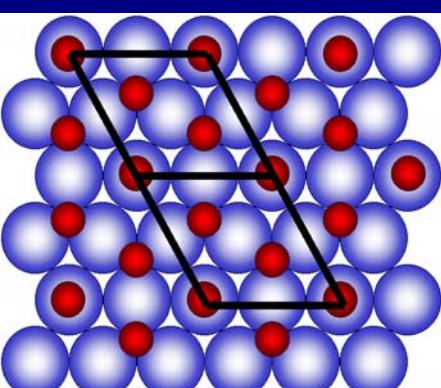
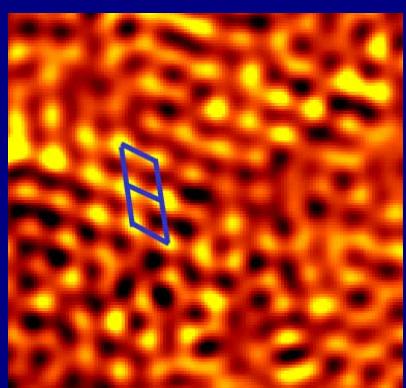
# CO-induced Ordered Structures during Poisoning of Ethylene Hydrogenation on Rh(111)



c(4x2)-C<sub>2</sub>H<sub>3</sub>+CO



(4x2)-3C<sub>2</sub>H<sub>3</sub>+CO



(2x2)-3CO

# Poisoning of Ethylene Hydrogenation by Carbon Monoxide

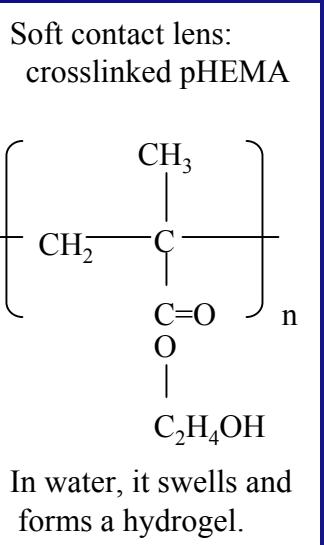
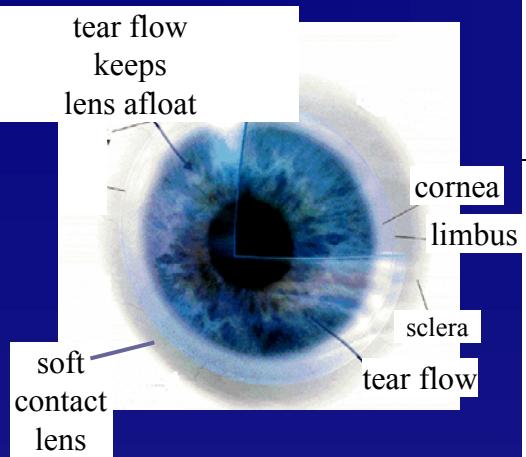
- 1) Mobility of Adsorbates on the Catalytically Active Surface
- 2) Mobility Stops and Formation of Ordered Surface Structure on the CO Poisoned Metal Surface

# Molecular Ingredients of Catalytic Activity

- Surface Structure
- Mobility of Metal Atoms, Adsorbates

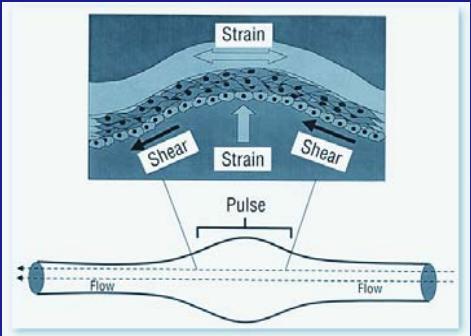
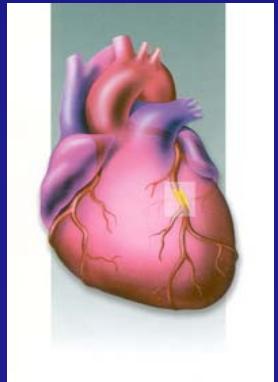
The Human Body is A  
Polymer-Water Interface System  
with Adsorbed Proteins

# a) Soft Contact Lens



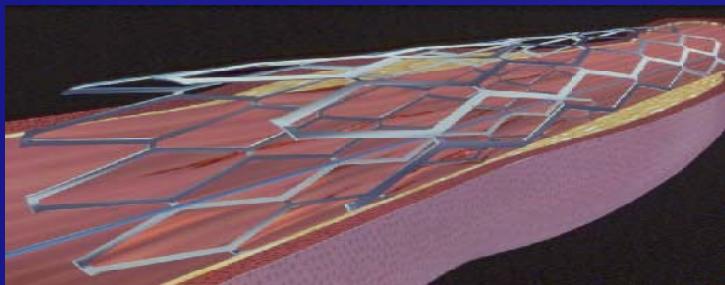
pHEMA = poly(2-hydroxyethyl methacrylate)

# c) Polyurethane Under Reversible Loading (Fatigue Test)

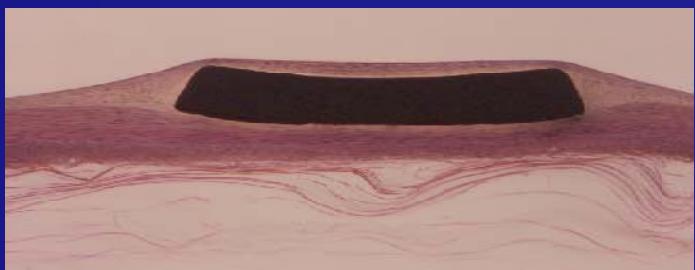


*3.2 billion heart valve loading cycles in  
~80 years of normal heart function.*

# b)

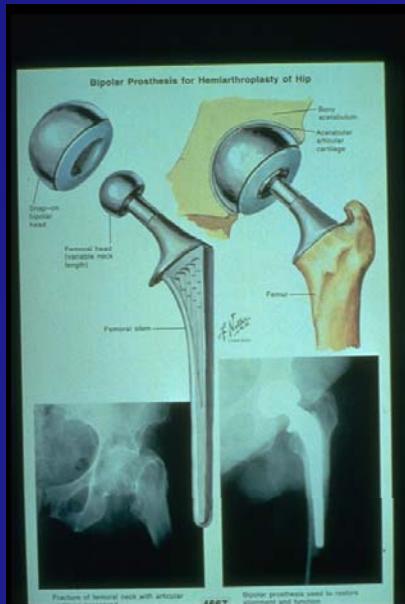


Stent

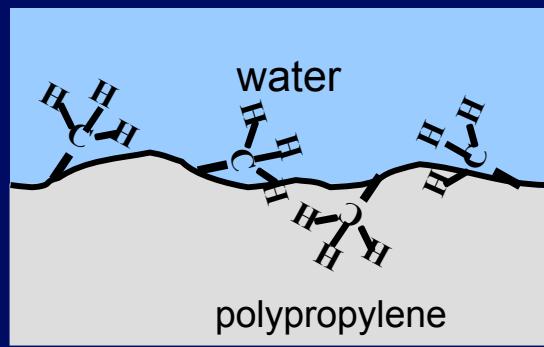
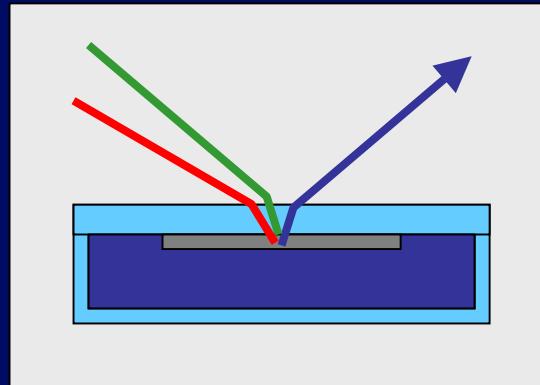
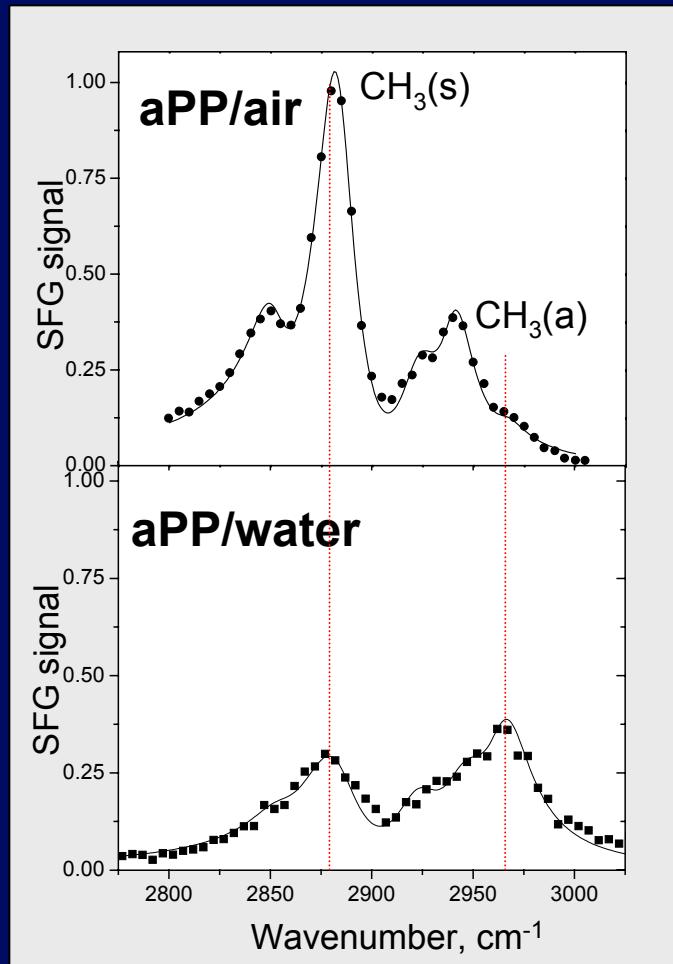


# d)

## Prosthesis



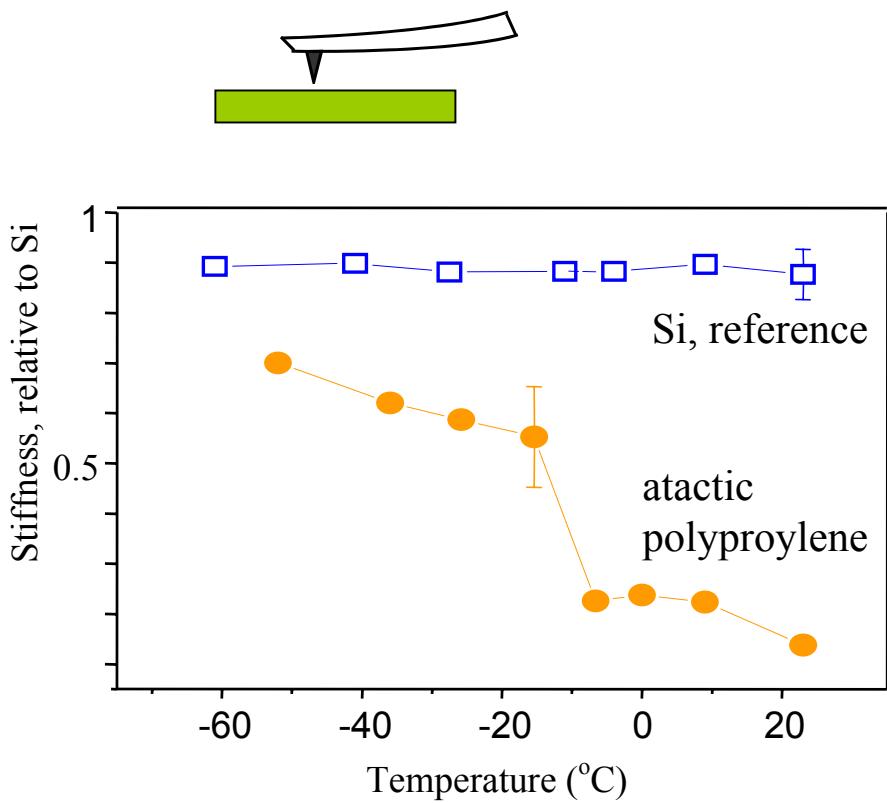
# Polypropylene/water interface



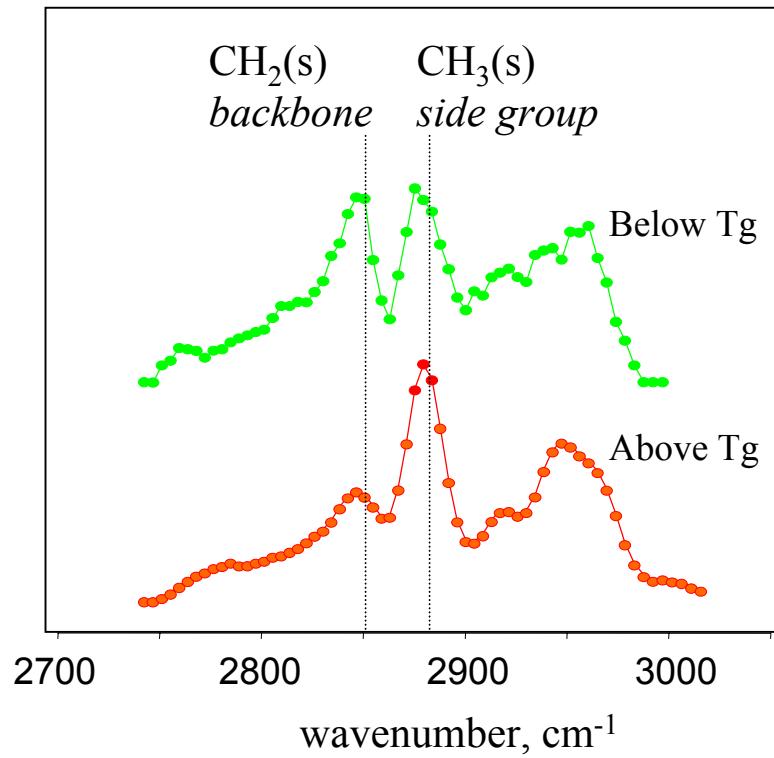
Polypropylene CH<sub>3</sub> side branches tilt and/or disorder

# Polypropylene glass transition, Tg

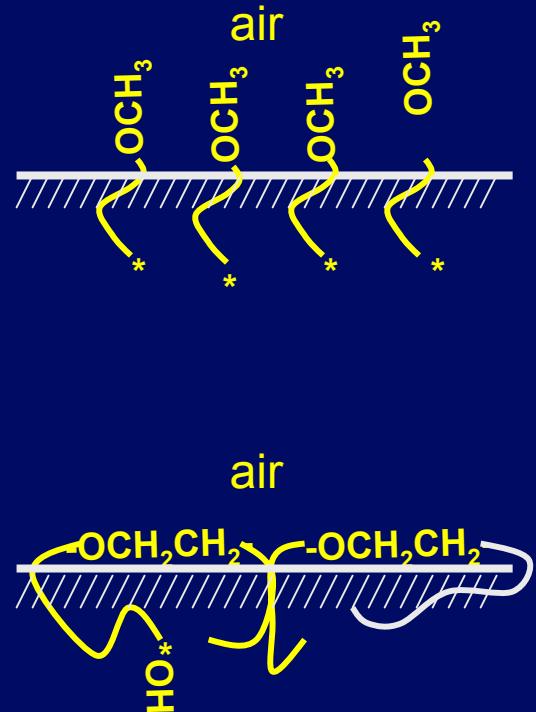
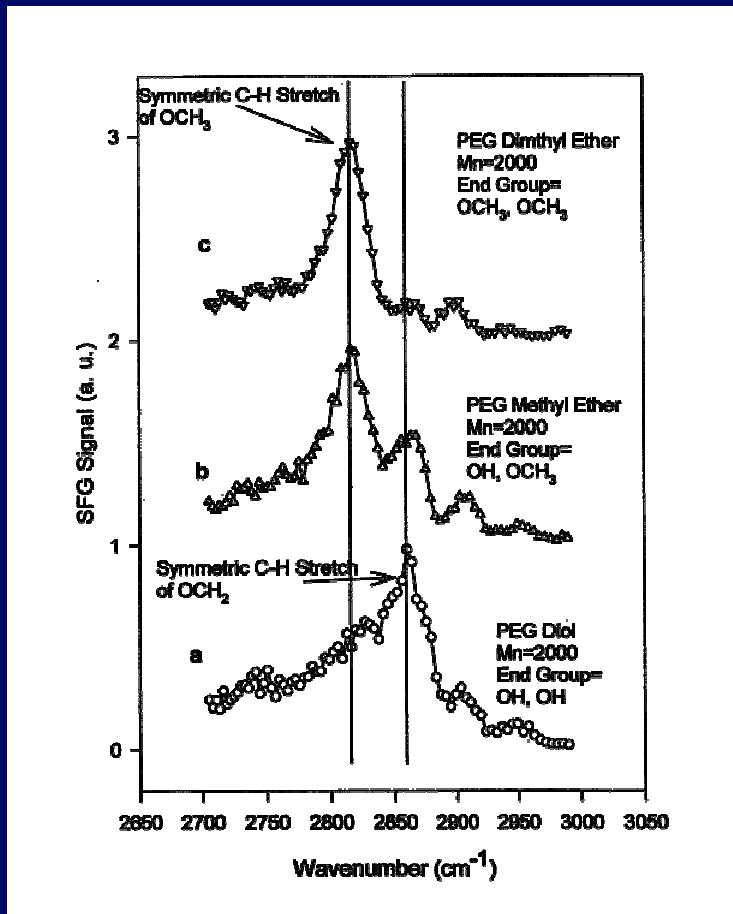
Stiffness, measured by AFM,  
increases below Tg



SFG shows changes in surface order  
-above Tg, pendant  $\text{CH}_3$  groups  
are ordered at surface  
-below Tg,  $\text{CH}_2$  backbone orders

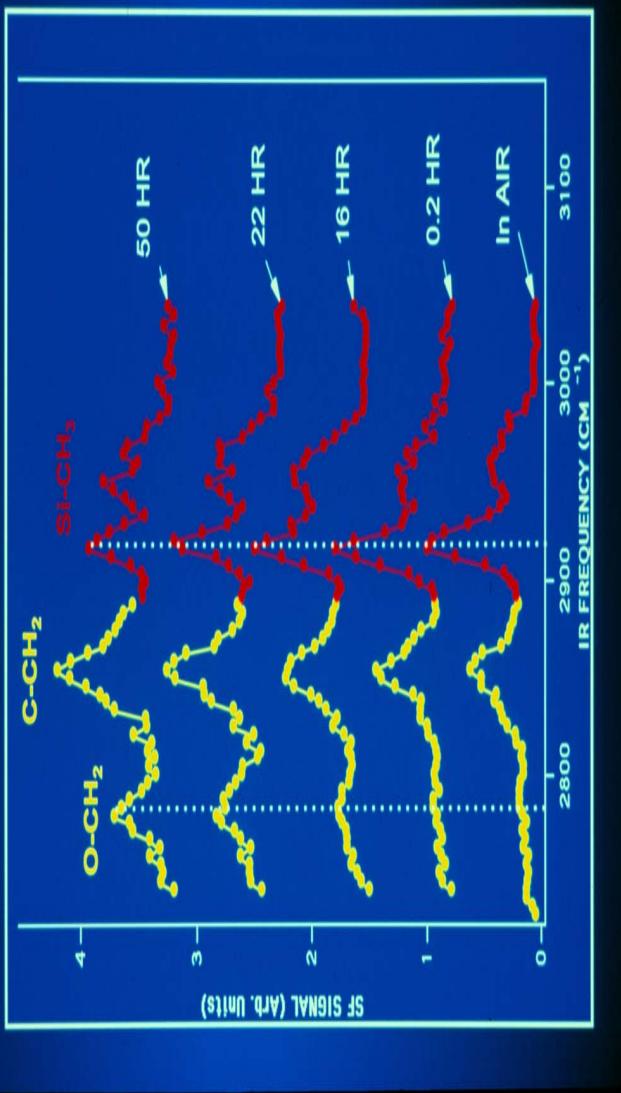


# Hydrophobic endgroup segregation at the air interface in polyethylene glycol (PEG) oligomers

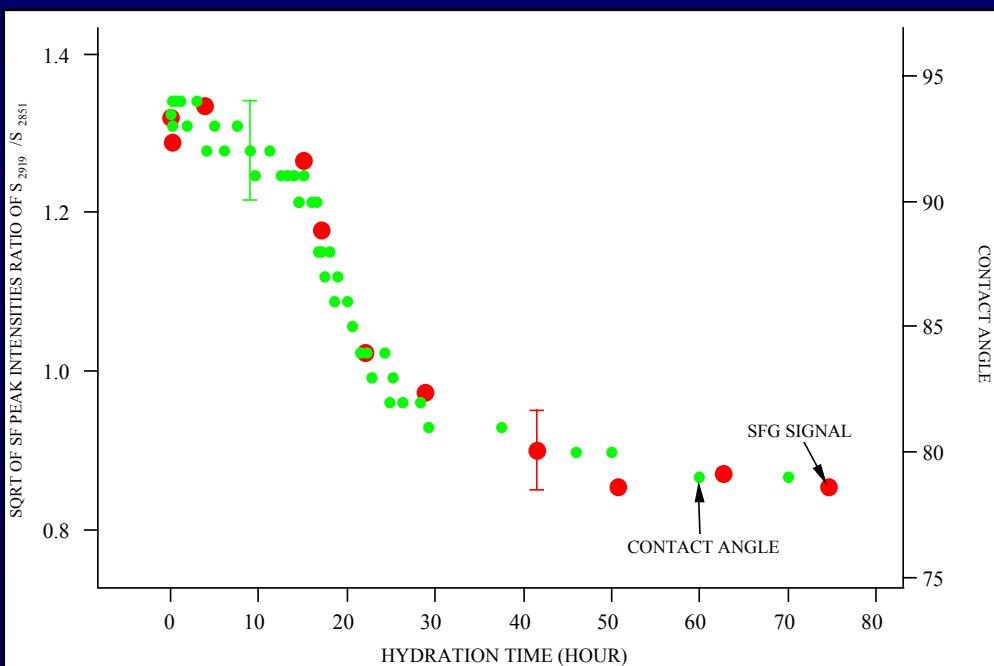


**Detection of Hydrophobic End Groups on Polymer Surfaces by Sum-Frequency Generation Vibrational Spectroscopy**  
Chen, Z.; Ward, R.; Tian, Y.; Baldelli, S.; Opdahl, A.; Shen, Y.-R.; Somorjai, G. A.;  
*J. Am. Chem. Soc.*; **2000**; 122(43); 10615-10620.

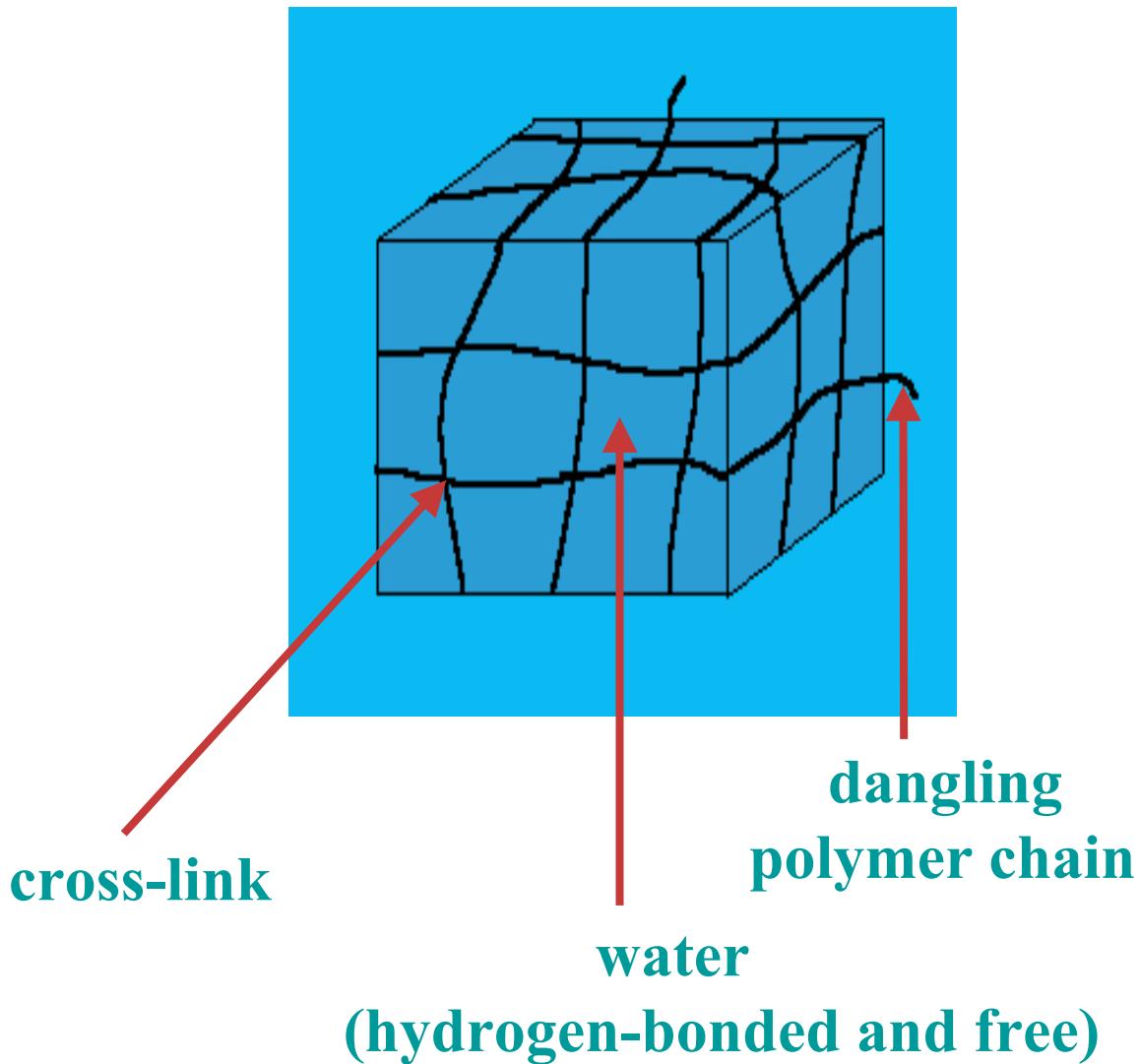
**Time Evolution of SFG Spectra at the Biospan-S/Water Interface**



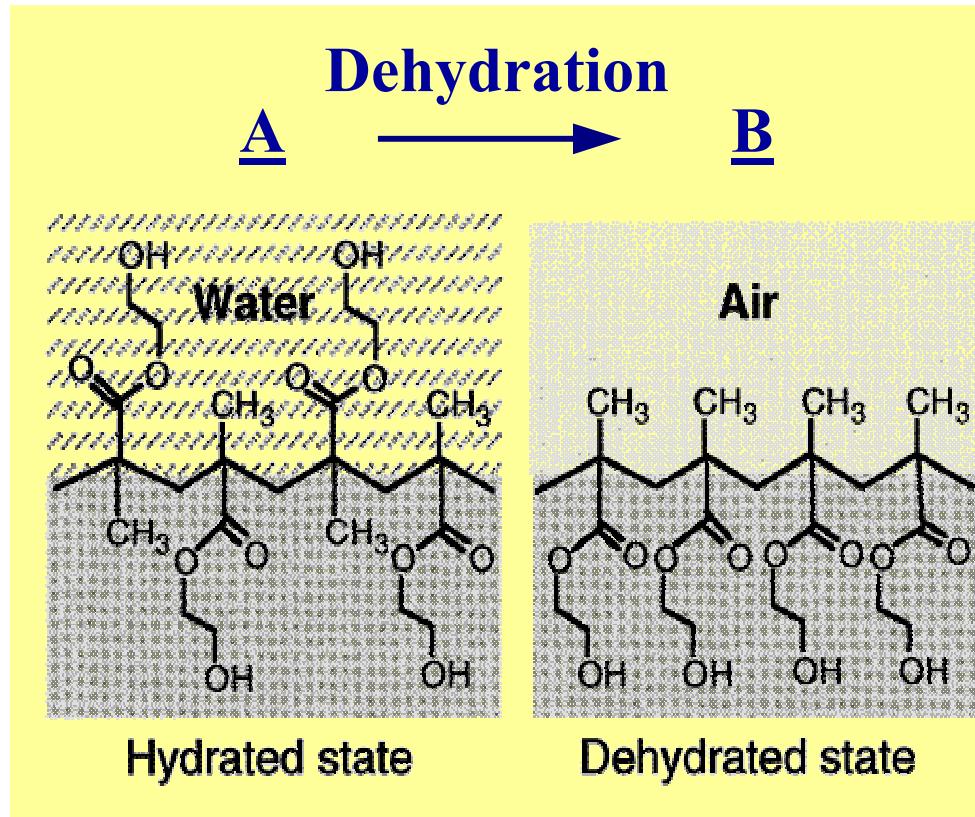
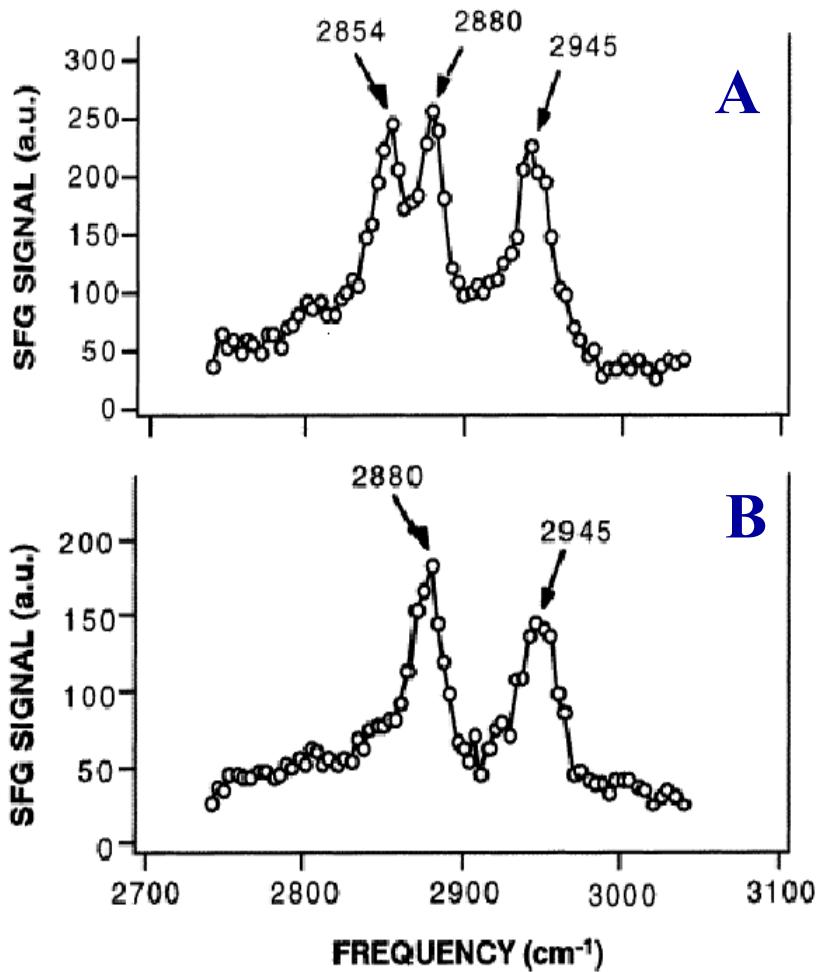
**SF Signal and Contact Angle vs. Hydration Time**



# Hydrogel Network



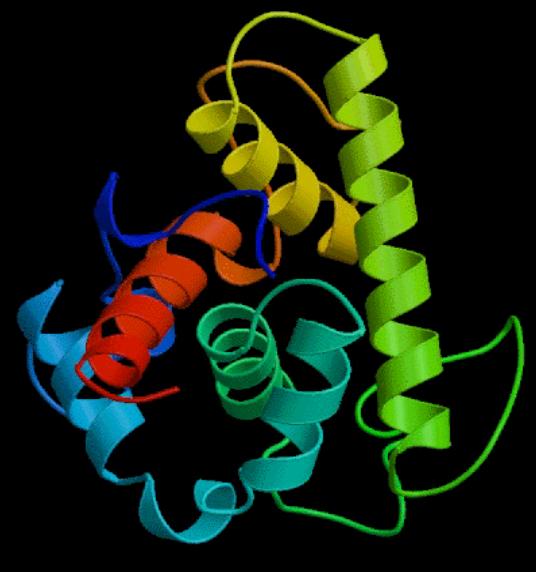
# Structural Rearrangement of pHEMA Hydrogel Surface



Chen, Zhang, Somorjai, and Bertozzi  
*J. Am. Chem. Soc.* **121**, 446 (1999)

# Proteins at Polymer Surfaces

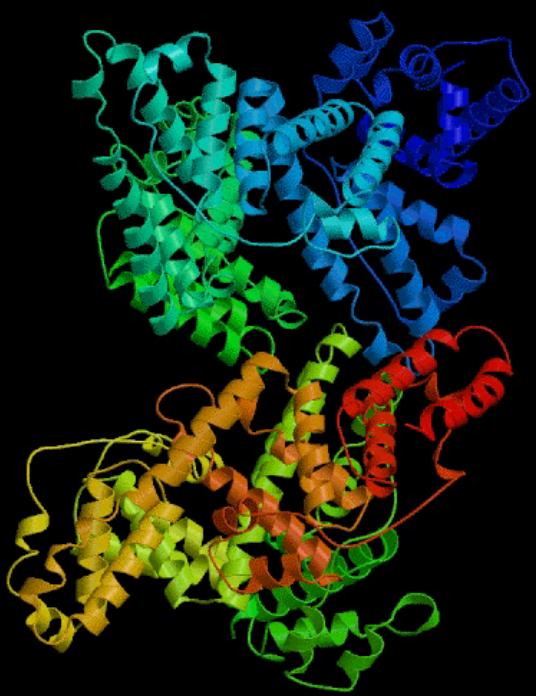
Hen Egg Lysozyme



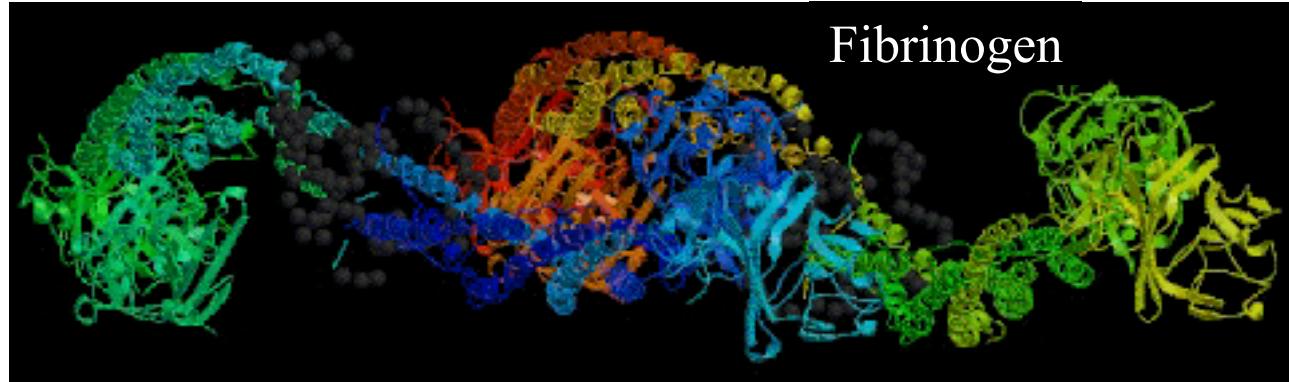
## Model Proteins

Proteins	MW	pI	Size (nm <sup>3</sup> )
Lysozyme	14,000	11.1	$5 \times 3 \times 3$
BSA	69,000	4.8	$8 \times 4 \times 4$
Fibrinogen	340,000	5.5	$47 \times 5 \times 5$

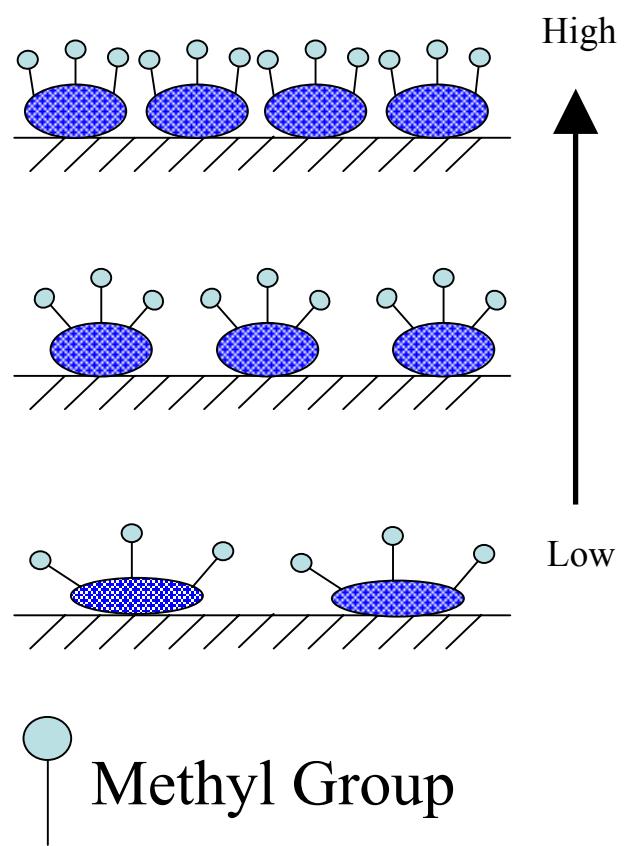
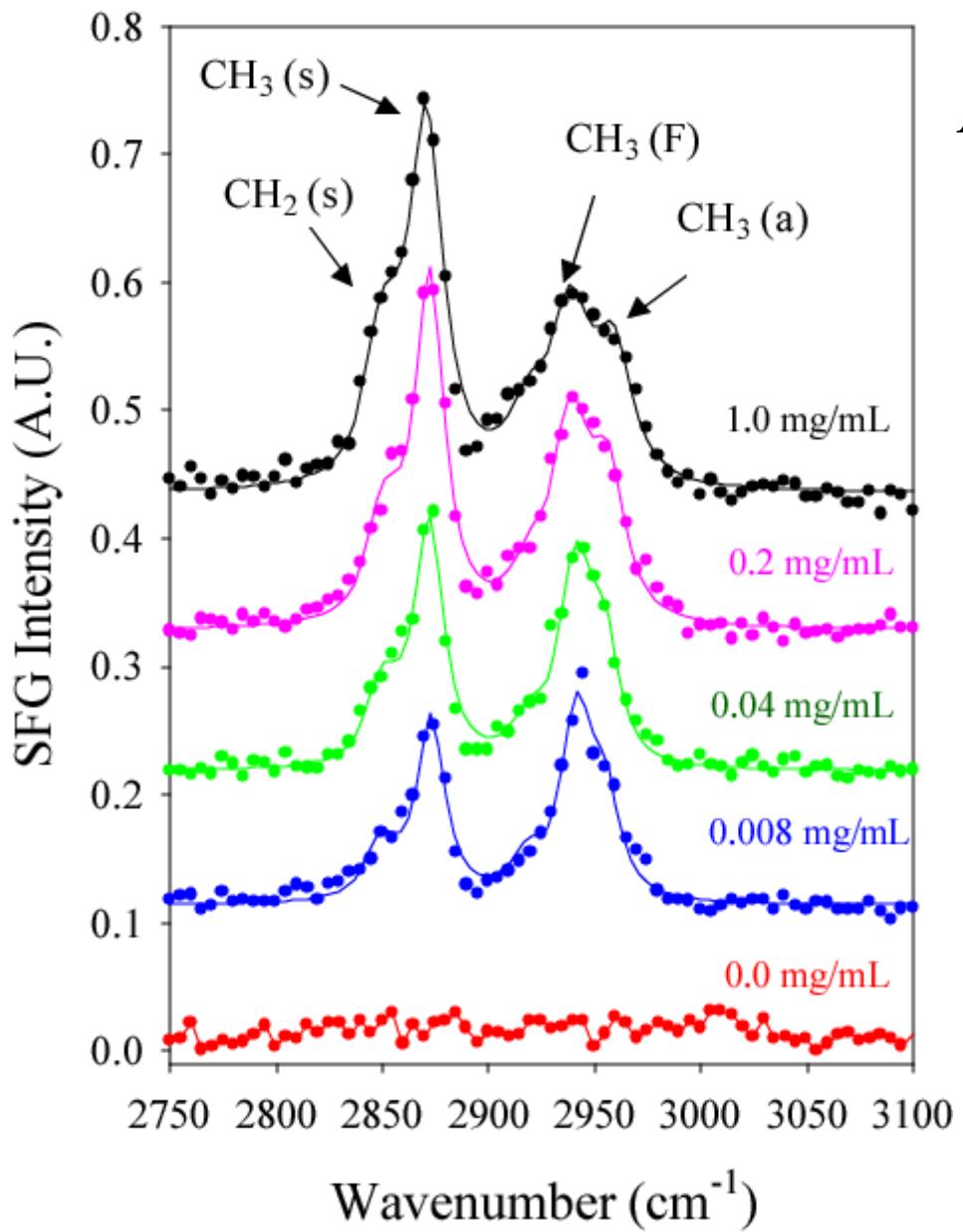
Bovine Serum Albumin



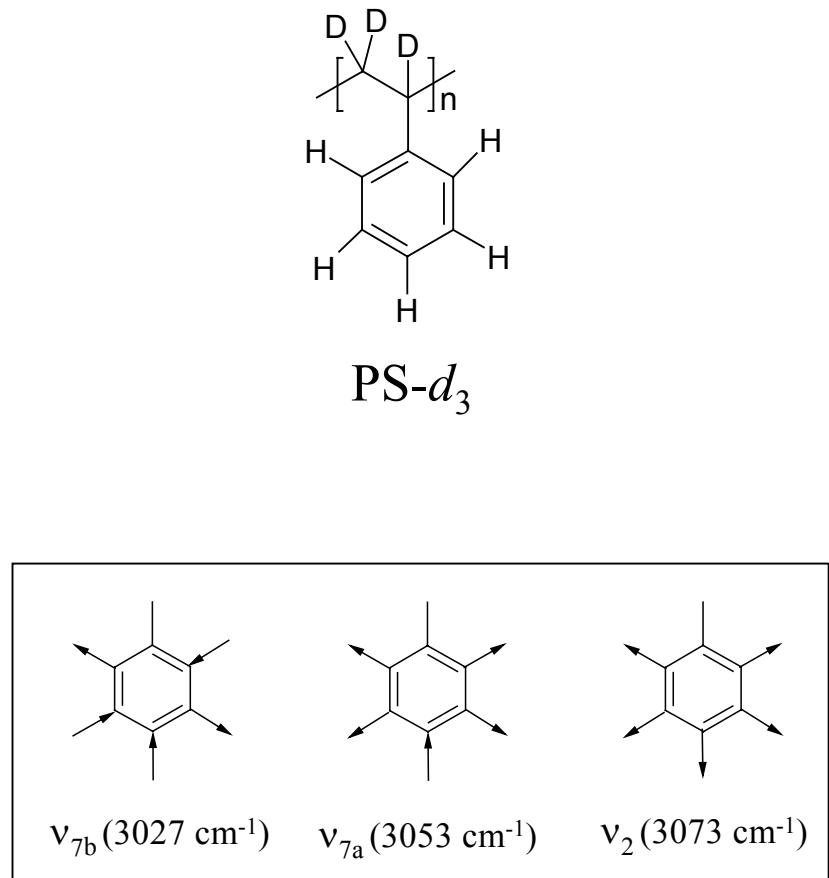
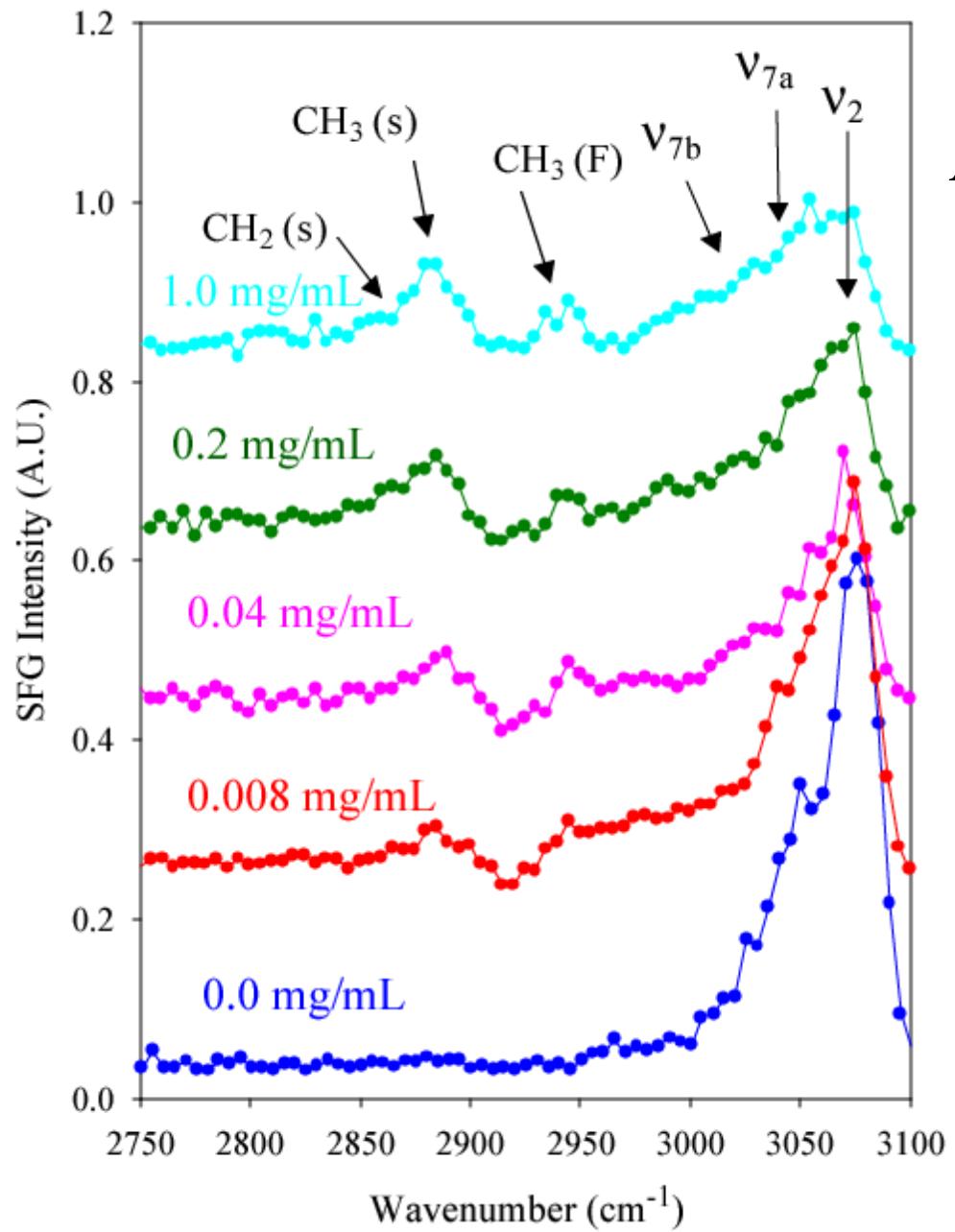
Lysozyme: Antibacterial Activity  
BSA: Hydrocarbon Carrier  
Fibrinogen: Blood Clotting



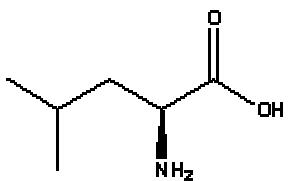
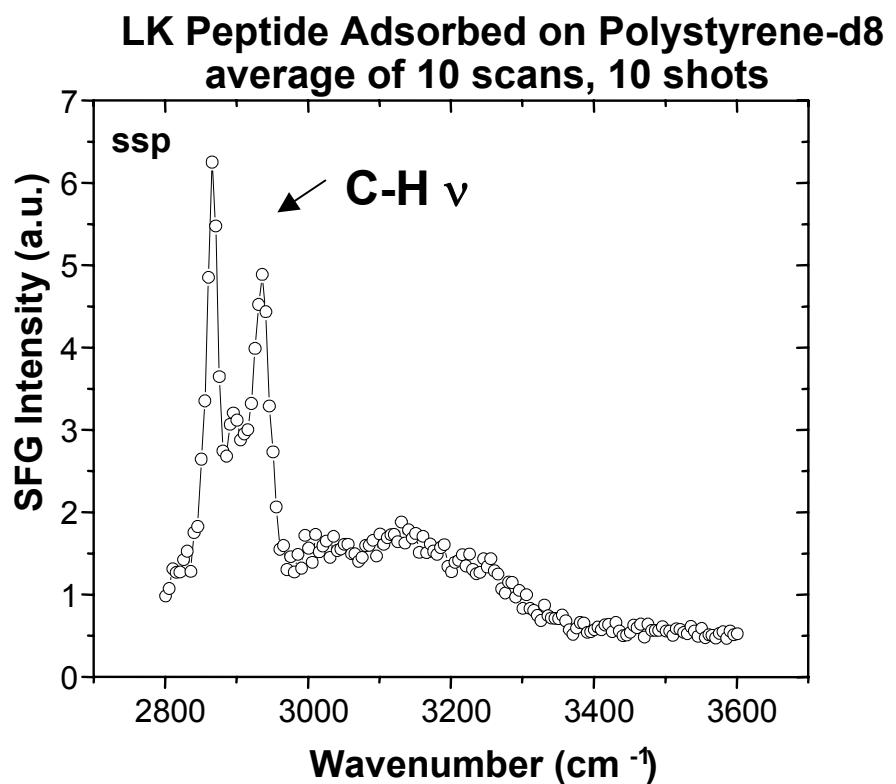
# SFG Spectra of BSA Adsorbed on Hydrophilic Silica Surfaces



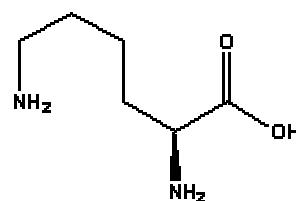
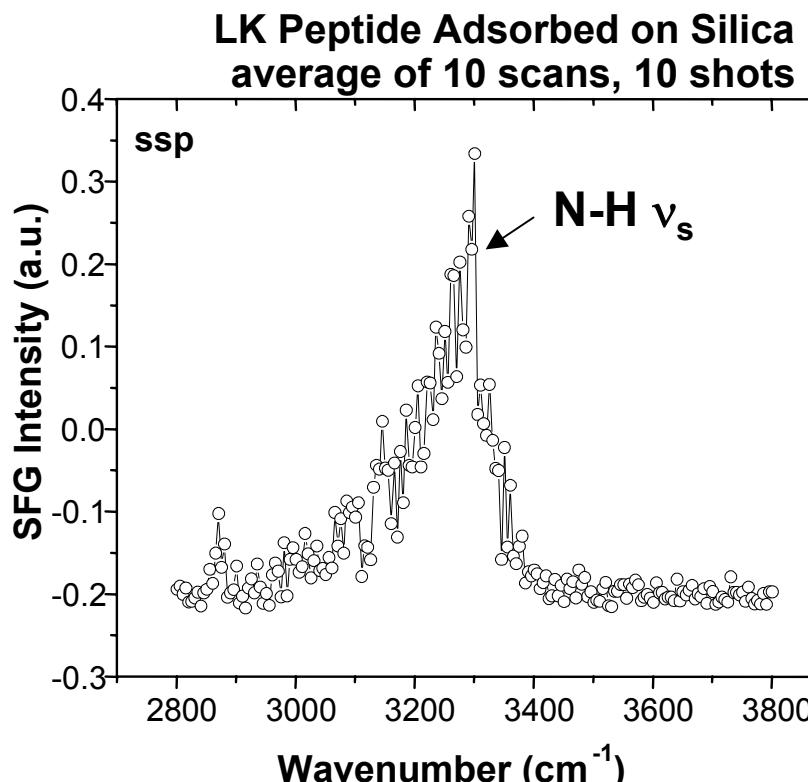
# SFG Spectra of Lysozyme Adsorbed on Hydrophobic Polystyrene Surfaces



# $\text{Ac}(\text{LKKLLKLLKKLLKL})\text{NH}_2$

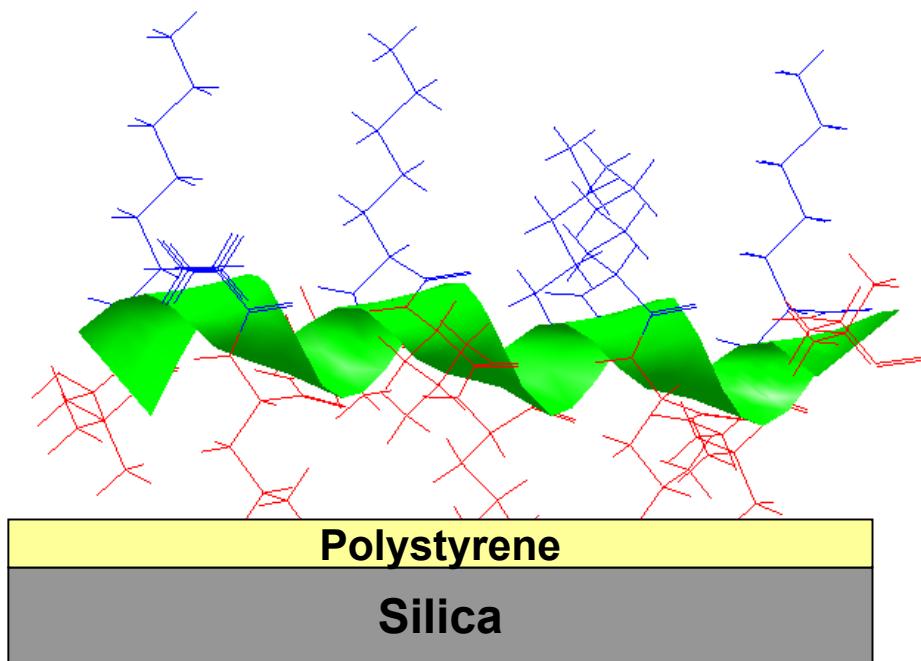


**L = Leucine**

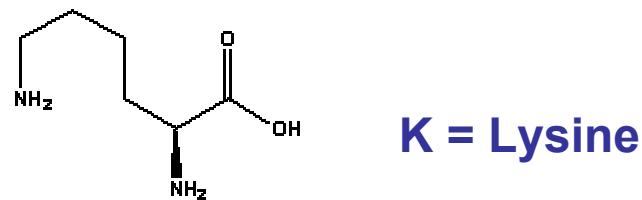
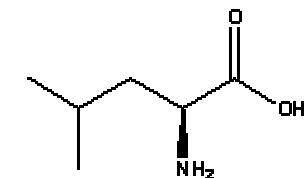


**K = Lysine**

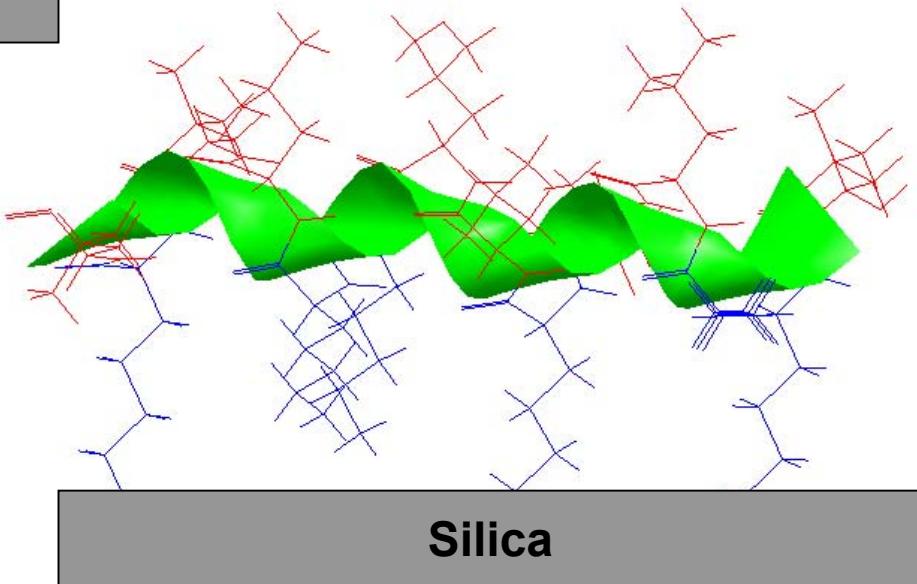
# LKKLLKLLKKLLKL Peptide Adsorption



**L = Leucine**



**K = Lysine**



# ALS Studies of Peptide and Protein Monolayers Adsorbed on Polymers

# Acknowledgement

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**Department of Energy, Basic Energy Sciences  
Chemical and Materials Sciences Divisions**